ROBERT A. TAFT WATER RESEARCH CENTER

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# A COMPARISON OF EXPANDED-BED AND PACKED-BED ADSORPTION SYSTEMS

ADVANCED WASTE TREATMENT LABORATORY-II

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FEDERAL WATER POLLUTION CONTROL ADMINISTRATION
OHIO BASIN REGION
Cincinnati, Ohio

# A COMPARISON OF EXPANDED-BED AND PACKED-BED ADSORPTION SYSTEMS

by

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for

The Advanced Waste Treatment Research Laboratory

Robert A. Taft Water Research Center

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# FOREWORD

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## ABSTRACT

The overall objective of this program was to evaluate the feasibility of the expanded-bed technique for contacting granular activated carbon with biologically treated sewage effluent, and to provide a rigorous comparison between this technique and the conventional packed-bed mode of operation. The evaluations and comparisons were to be made with pilot scale adsorbers under actual field operating conditions. Although secondary effluent without further pretreatment was of primary interest, the effects of additional clarification were also to be determined. Clarification methods included dual media filtration and chemical treatment followed by dual media filtration.

The packed-bed and expanded-bed adsorption systems, operating under comparable conditions, were found essentially equivalent in their effectiveness for removal of soluble organic material from a secondary sewage effluent. Suspended solids, present to some degree in all the wastewaters tested, were more effectively removed by the packed beds. The expanded beds did, however, remove some suspended material. Accumulation of suspended solids caused rapid increase in head loss in the packed beds, necessitating frequent cleaning of the carbon in these beds. Cleaning was carried out by air agitation and back washing of the beds. Suspended material accumulated on individual carbon granules in the expanded beds creating larger particles of decreased density. Although there was no head loss associated with this behavior, there was increased expansion of the bed. When such expansion became excessive, the beds had to be cleaned. However, the expanded beds required much less frequent cleaning than did the packed beds.

Because the expanded beds are not subject to clogging from accumulated solids, their pumping power and maintenance requirements are lower than for a packed bed of the same size. Where the improved suspended solids removal provided by a packed bed is not required, the expanded-bed adsorber may be preferred.

# INTRODUCTION

The demand for more stringent protection of our national water resources from the degradation of pollution has mounted steadily in recent years. Concurrently, increases in population and improvements in standard of living have placed a heavy burden on the diminishing supply of high-quality water. As a result, much emphasis has centered on the improvement of the quality of wastewater discharged into streams, rivers, lakes, and other receiving waters. Considerable effort has been expended in research to improve conventional wastewater treatment techniques. Cognizant of future requirements as well as of the immediate needs, the Federal Water Pollution Control Administration and others[1] are conducting major research, development, and demonstration programs for new processes which will provide the higher levels of treatment required for those situations where conventional treatment processes are inadequate.

One area of investigation in which promising results have been achieved has been the removal of persistent organic materials by adsorption on activated carbon. Persistent organic compounds are those which remain in the wastewater even after conventional secondary treatment. Several large-scale studies on carbon treatment of waste waters are presently underway in this country. Notable among these are the studies at Lake Tahoe[2] and Pomona,[3] California, where packed-bed carbon contacting systems are being utilized. A packed-bed system is also being used in Nassau County, New York, where adsorption on granular activated carbon is one of a series of processes being used to treat secondary sewage effluent to produce water of satisfactory quality for recharging ground water aquifers.[4] The use of powdered activated carbon for renovation of secondary effluent has been studied at several locations,[5,6] including the FWPCA's Lebanon, Ohio, pilot plant operated by the Cincinnati Water Research Laboratory.

Packed beds of granular activated carbon are well suited for treatment of liquids that contain little or no suspended solids, and with a clear feed can be expected to operate effectively for extended periods without clogging or excessive pressure loss. However, the presence of suspended solids in municipal wastewaters presents some problems for the use of activated carbon in packed beds. These solids lead to progressive clogging of the beds, much as in a sand filter, with resulting increases in head loss. At the Pomona installation the filtering action of packed beds of activated carbon is actually used as part of the treatment scheme. In this system the first of four activated carbon beds operating in series serves as a filter to provide a clear feed to the three subsequent beds. Suspended solids are removed from the first bed daily by surface washes and backwashing. The Lake Tahoe and Nassau County systems include pretreatment of secondary effluent by chemical clarification

and filtration to provide a highly clarified feed permitting extended operation of the carbon beds.

The work reported here has been directed toward field evaluation of expanded-bed adsorbers, which have certain potential operating advantages over packed-bed adsorbers for treating solutions which contain suspended solids. By passing water to be treated upward through a bed of activated carbon at a velocity sufficient to expand the bed, problems of plugging of the bed and increasing pressure drop are eliminated. Effective operation over longer periods of time results, as clearly demonstrated previously in comparative laboratory studies and preliminary short-term, small-scale field studies of expanded-bed adsorbers.[7] Another advantage of the expanded bed is the lack of dependence of pressure drop on particle size. In an expanded bed it is possible to use carbon of smaller particle size than is practical in a packed bed, thus taking advantage of the higher adsorption rates which obtain for smaller particles. The purpose of the present work has been to extend preliminary field studies to operationally more meaningful field evaluations and to provide comparisons on a practical scale and for extended periods.

## SUMMARY

After a preliminary program of laboratory studies to provide information required for the design of a pilot plant, field studies of the expanded-bed and down-flow packed-bed adsorption systems were performed. In these field studies, packed-bed and expanded-bed adsorbers were compared in parallel using a biologically treated secondary sewage effluent from the Ewing-Lawrence, (New Jersey,) Sewerage Authority trickling filter treatment plant, for feed to the systems. Although secondary effluent without further treatment was used for some of the work, the effects of additional clarification were also studied. Clarification methods included dual media filtration, and chemical clarification followed by dual media filtration. For all studies, a flow rate of 5 gpm/ft$^2$ was employed. Adsorption column diameters were either 6 in. or 10 in. Carbon depths for most of the studies were either 12 ft or 24 ft. Carbon used in the packed beds was a commercially available product having a size range of 12x40 mesh. Carbon in the same size range, and in a finer size range obtained by screening and crushing to 20x40 mesh, was used in the expanded beds.

The packed-bed and expanded-bed adsorption systems were found to be essentially equivalent as far as effectiveness of removal of soluble organic carbon from each of the differently treated effluents was concerned. For the same carbon particle size, packed beds theoretically should be more effective if the carbon is not mixed during operation. Because of the need for frequent backwashing of packed beds, this advantage is lost.

Suspended solids, remaining to some degree in all of the differently pretreated sewage effluents, were partially removed in the packed-bed adsorbers, leading to clogging and increased head loss. These increases in head loss required frequent cleaning of the packed beds by air agitation and backwashing. The expanded-bed adsorbers also served to remove some of the suspended solids, although to a smaller degree than did the packed beds. The suspended solids removed in the expanded bed tended to surround the individual particles of carbon in a relatively uniform film. This film had no apparent effect on the adsorption process, nor was there any problem with increases in head loss in the expanded beds as there was in the packed beds. The only apparent adverse effect of the solids which accumulated on individual carbon granules in the expanded bed was a decrease in the effective density of the encapsulated carbon particles which caused an increased expansion of the bed. Thus, it was necessary periodically to clean the expanded bed when the expansion became excessive. The required cleaning frequency of the expanded beds, however, was only about 1/3 to 1/4 as great as that for the packed beds.

The films that developed around the particles in the expanded beds had the appearance of biological slime; these films might have functioned to trap some of the smaller suspended solids from the wastewater moving through the beds. Carbon beds serve as a rather favorable environment for development of biological growth, probably because of the concentration of organics by the carbon. The fact that this growth environment is somewhat unique to activated carbon beds was confirmed in the present work by parallel experiments with coal and activated carbon beds, identical in all respects except the composition of the solid media. Abundant growth occurred on the activated carbon particles but none on the coal particles. The extent of the removal of soluble organics which might have been accomplished by strictly biological action, rather than by adsorption, is difficult to estimate. However, it is probably very small since no real differences were noted between the removal rate with increased accumulation of solids in the adsorbers, and that after air scouring and cleaning of the carbon to remove most of the attached biological growths.

The results of all of the experiments conducted under this program point to the conclusion that expanded-bed adsorbers can provide about the same degree of removal of organic substances from secondary sewage as can packed-bed adsorbers, but at lower operating pressures and with significantly less down-time and cleaning cost. These advantages of the expanded-bed adsorber should permit activated carbon treatment by this technique at a cost several percent below that of the packed-bed technique.

The fact that the packed bed removed somewhat more of the suspended solids would not appear to be a very significant factor. On this effluent, neither system was completely satisfactory. If a low level of suspended solids is required, it would be necessary to add additional clarification treatment to each of the two adsorption systems. The notable advantage of the expanded-bed technique in this regard is that the clarification step could follow the adsorption step, thus providing for removal of solids which might be generated in the adsorption column. As mentioned previously, there is a notable tendency for biological growth to develop in the carbon adsorbers, both packed and expanded. Clarification could, of course, be added after a packed-bed adsorber, but this would not solve the problem of clogging and fouling of the adsorber.

## RECOMMENDATIONS

When adsorption on activated carbon is to be used for advanced treatment of secondary effluent, serious consideration should be given to the expanded-bed concept of contacting.

Observations made during this investigation suggest that the expanded-bed method of contacting activated carbon may be very effective for the treatment of raw sewage; therefore, further studies should be conducted to evaluate the expanded-bed contacting system for removal of organics from raw sewage or primary effluent.

Detailed design and cost analysis of an expanded-bed contacting system should be made.

A program should be carried out to develop an expanded-bed contacting system with provision for continuous addition of fresh carbon and removal of spent carbon.

## PRELIMINARY LABORATORY INVESTIGATIONS

Preliminary laboratory studies were conducted to examine the sorptive properties and physical characteristics of the carbon to be used in the pilot field study, and to provide appropriate design and operating information relative to the expanded and packed-bed systems to be field tested in the pilot-scale phases of the program. These preliminary laboratory studies were divided into two principal categories: hydraulic characteristics of the experimental expanded-bed adsorbers, and properties of the activated carbon to be used in the experiments.

### HYDRAULIC CHARACTERISTICS

The expanded-bed concept for contacting wastewater with activated carbon calls for the maintenance of a semi-fluidized bed of particles with relatively uniform distribution and motion of the particles throughout the bed. If there is a very wide distribution of particle sizes of carbon in such a system, it is quite possible that the smallest particles will be carried over in the effluent stream at flow velocities just sufficient to cause expansion of the largest particle size fractions. This suggests the desirability of a relatively narrow range of particle sizes. The importance of particle size range was the factor to be determined in the preliminary laboratory investigations. Parameters affecting the hydraulic behavior of the bed include particle size, shape, and density; velocity; properties of the fluid; and the presence of suspended matter in the fluid.

The preliminary hydraulic studies were conducted with tap water in a 9-ft high, 6-in. diameter glass column, as shown in Figure 1. The column was suspended and adjusted to plumb by reference to a precision level, and maintained in a vertical position during the course of all operations and measurements. The bottom of the column was fitted with a cone distributor which was covered, for the major part of the test, by a 6-in. bed of gravel. Granular activated carbon* that had been thoroughly soaked in water for up to three days was placed in the water-filled column to give a settled bed of about 4-ft depth. Water was then pumped upward through the bed to expand gently the carbon and expel air bubbles and remaining fines before any measurements were made. During each test, water was pumped fror a supply reservoir through a rotameter into the bottom of the column, upward through the bed and back to the supply reservoir. The temperature of the water in the system was maintained relatively constant by appropriate additions of either hot water or ice to the supply reservoir.

Three different particle-size ranges and several different flow rates were tested at controlled water temperatures of 10°C,

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*Pittsburgh CAL (Calgon Filtrasorb) activated carbon was used as received or after particle size reduction for all studies described in this report. This carbon is manufactured by the Pittsburgh Activated Carbon Company, a subsidiary of the Calgon Corp.

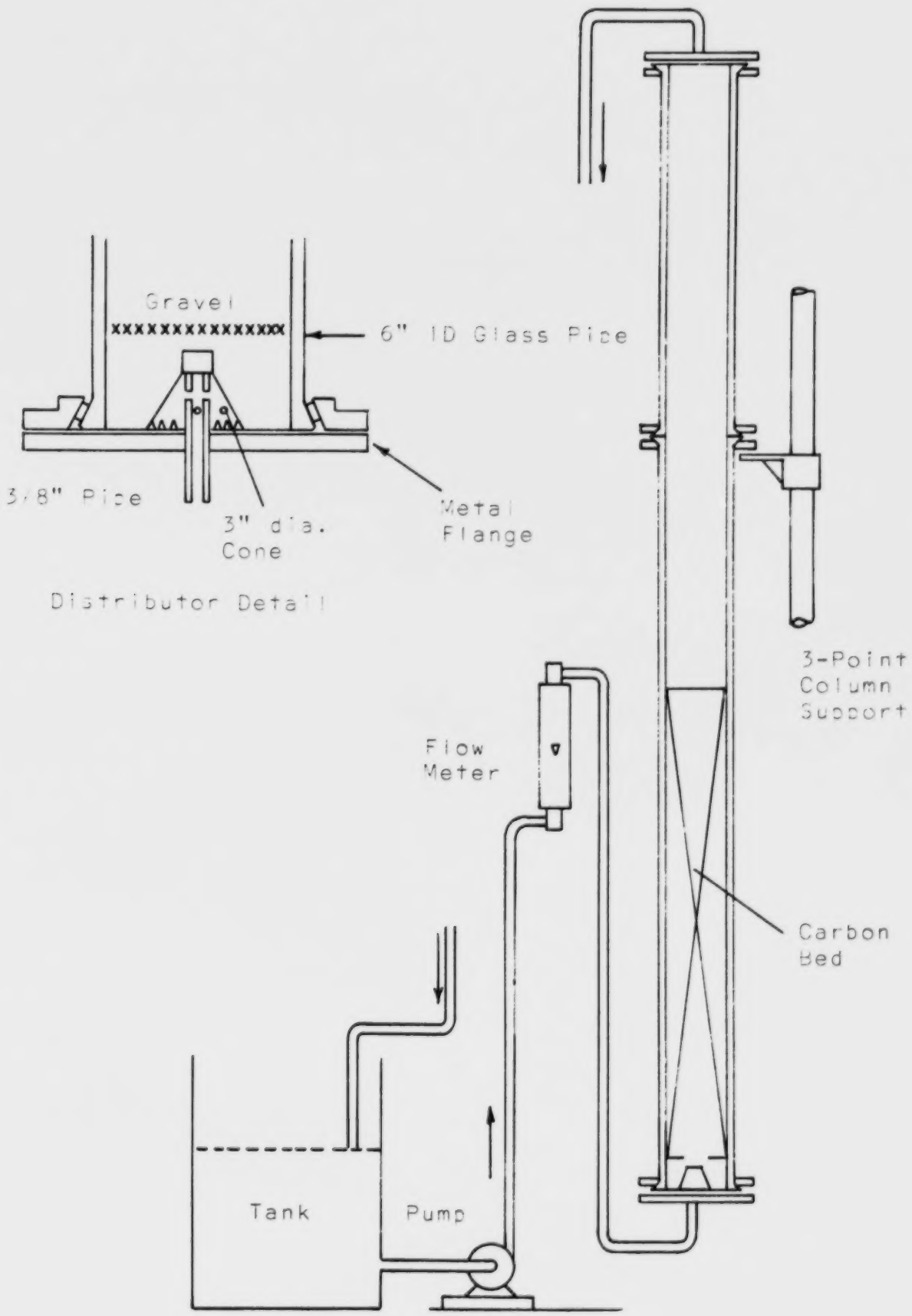


FIGURE 1. APPARATUS FOR GLASS COLUMN EXPERIMENTS

20°C, and 25°C. All of the carbon tested was taken from the same batch as that to be used for the pilot-scale field studies. The appearance of the bed was noted, and the heights of various regions of particle activity were measured. The different patterns of particle behavior observed in the column are described as static, when no particle motion was evident; moving, when particles were moving slowly over short distances; and mixing, when there was considerable random and relatively rapid particle motion. The top of the expanded bed of carbon was very clearly defined at all times during these tests, and remained perfectly flat. Conversely, the lines of demarcation between the mixing and moving regions and between the moving and static regions were rather poorly defined, and generally irregular. Different types of particle motion on different sides of the column were frequently observed, and, in some cases, channeling was noted over rather limited areas. The plot of the data, Figure 2, provides a graphical comparison of the behavior of the different particle size fractions used in the experiments. The 12x40* range represents the particle size distribution in the commercial product as supplied by the manufacturer. The 20x30* and 20x40* sizes were obtained by crushing and screening the commercial product.

The 12x40 particles were tested with two types of fluid distributors in the bottom of the column. The first distributor system consisted only of the 3-in. inverted cone mentioned earlier, which provided for the water to enter the column through holes in the circumference of the cone. The second distributor consisted of the same cone set in a 6-in. deep bed of gravel, as illustrated in Figure 1. The results from the experiments with the two different distributor systems were essentially the same, and the gravel support was used for all subsequent tests.

As expected, a greater expansion was observed with the mixtures containing smaller particles. The bed expansion approached 200% at about 7 gpm/ft$^2$ for the 30x40 size range and at about 10 gpm/ft$^2$ for the 20x40 size range. At the chosen experimental rate of 5 gpm/ft$^2$, the 20x40 particles gave a bed expansion of about 130%, of which about 75% of the bed was moving. This particle size range was selected along with the commercial 12x40 carbon for use in the pilot study, rather than the finer 30x40 size which might have resulted in excessive loss of carbon particles during the experiment.

## CARBON PROPERTIES

As previously noted, the activated carbon obtained from the manufacturer consisted of particles in the size range 12x40, with a considerable fraction of these particles being in the 12x20 category. Several methods of fractionation and size reduction were tested in an effort to develop a procedure for producing maximum yield of the 20x40 size carbon particles selected for use

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*12x40 means particles passing a U.S. Standard Sieve No. 12 and being retained on a U.S. Standard Sieve No. 40; 20x30 means passing a No.20 sieve, retained on a No. 30 sieve; and, 20x40 means passing a No. 20 sieve, retained on a No. 40 sieve.

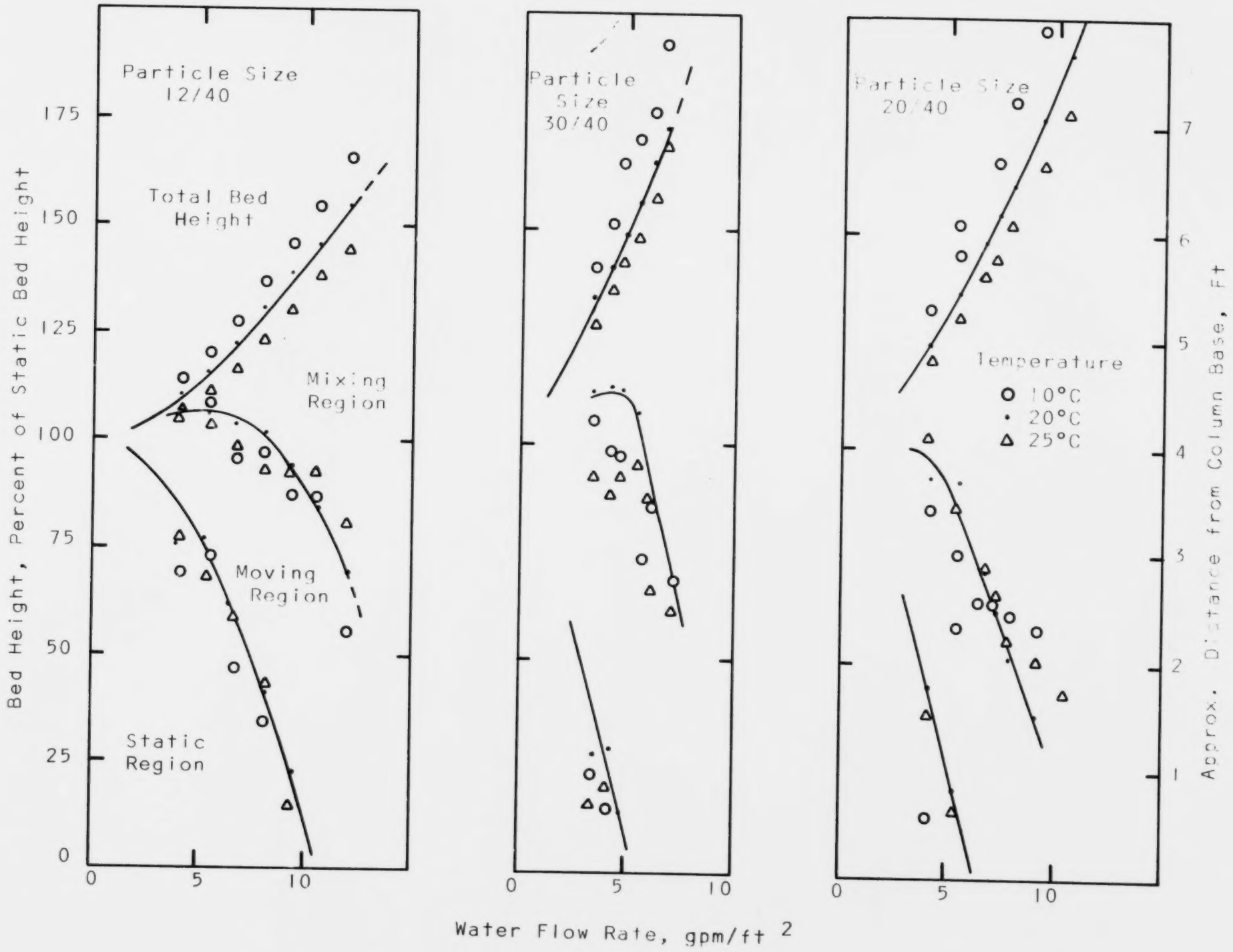


FIGURE 2. BEHAVIOR OF EXPANDED BEDS OF ACTIVATED CARBON

in the pilot study. The method finally chosen made use of batch screening and a jaw crusher which, after appropriate modifications, was capable of converting about 60% of the 12x40 carbon to 20x40 without excessive fines. Particle-size analyses of the carbon were conducted with 50 to 100 gram samples shaken for 10 minutes in 8-in. U.S. Standard Sieves in a Ro-Tap machine. A small amount of 30x40 carbon was prepared for the preliminary tests, and then sufficient 20x40 was prepared to fill the four pilot columns, which held about 85 pounds each. The remaining 40% of the original carbon obtained from the manufacturer was discarded either as fines or as over-size carbon.

For meaningful evaluation of the relative effectiveness of the packed-bed and expanded-bed adsorption systems, the carbons used in the two types of systems had to have very nearly identical adsorption properties. Measurement of iodine adsorption was the principal test used to determine the effects of the crushing and size-separation operations on the adsorption properties of the experimental carbon. These tests shown in Table 1 indicated that crushing of the carbon resulted in a somewhat lower activity for the plus-20 granular fraction remaining after crushing and sieving and a fairly high activity in the dust produced during crushing. Similarly, slight differences were noted between the activity of the coarse and fine particles of the original carbon. Differences between the activities of coarse and fine particles in a batch of granular activated carbon are not at all uncommon. In many cases, these differences are accentuated when the particles are further processed by grinding, crushing, or rough sieving. The more active particles are generally structurally weaker, and are therefore more readily crushed or abraded to yield powder-like fines, while the harder and more dense, but less active, particles are more resistant to abrasion and crushing.

While the iodine-adsorption procedure does serve as a convenient method for rapidly estimating the gross adsorption properties of an activated carbon, a realistic evaluation of the characteristics of a carbon with respect to sorption of organic matter from wastewater requires a more directly related measure of the specific property. For this reason, equilibrium adsorption tests with a filtered secondary sewage effluent were conducted on pulverized samples of the different particle size fractions of the activated carbon. These tests involved the mixing of 100-ml samples of the filtered secondary effluent with different quantities of the pulverized activated carbon for one hour, after which the carbon was allowed to settle. The supernatent was then filtered and the total concentration of organic carbon* determined on the filtrate. The organic carbon remaining was compared with the total concentration of organic carbon in another portion of the effluent to which no carbon had been added. The results of these experiments are presented as Freundlich isotherms in Figure 3. The comparison shows no consistent difference in capacity for adsorption of organic carbon among the different size fractions of the activated carbon prepared from the original 12x40 commercial product. These

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*Determined using a Beckman Carbonaceous Analyzer

TABLE 1

Iodine Numbers of Activated Carbon

| Batch No. | 1 | 2 | 3 | 4 |
|---|---|---|---|---|
| Total 12x40 | 950 | 915 | 915 | 962 |
| Minus 40 | 985 | 960 | 962 | 981 |
| Plus 20 | 950 | 830 | 840 | 834 |
| 20x40 | 965 | 930 | 942 | 934 |
| 30x40 | 962 | | | |

Iodine No. is mg I adsorbed per gm of carbon from 50 ml 0.1 N iodine solution by 0.5 gm carbon

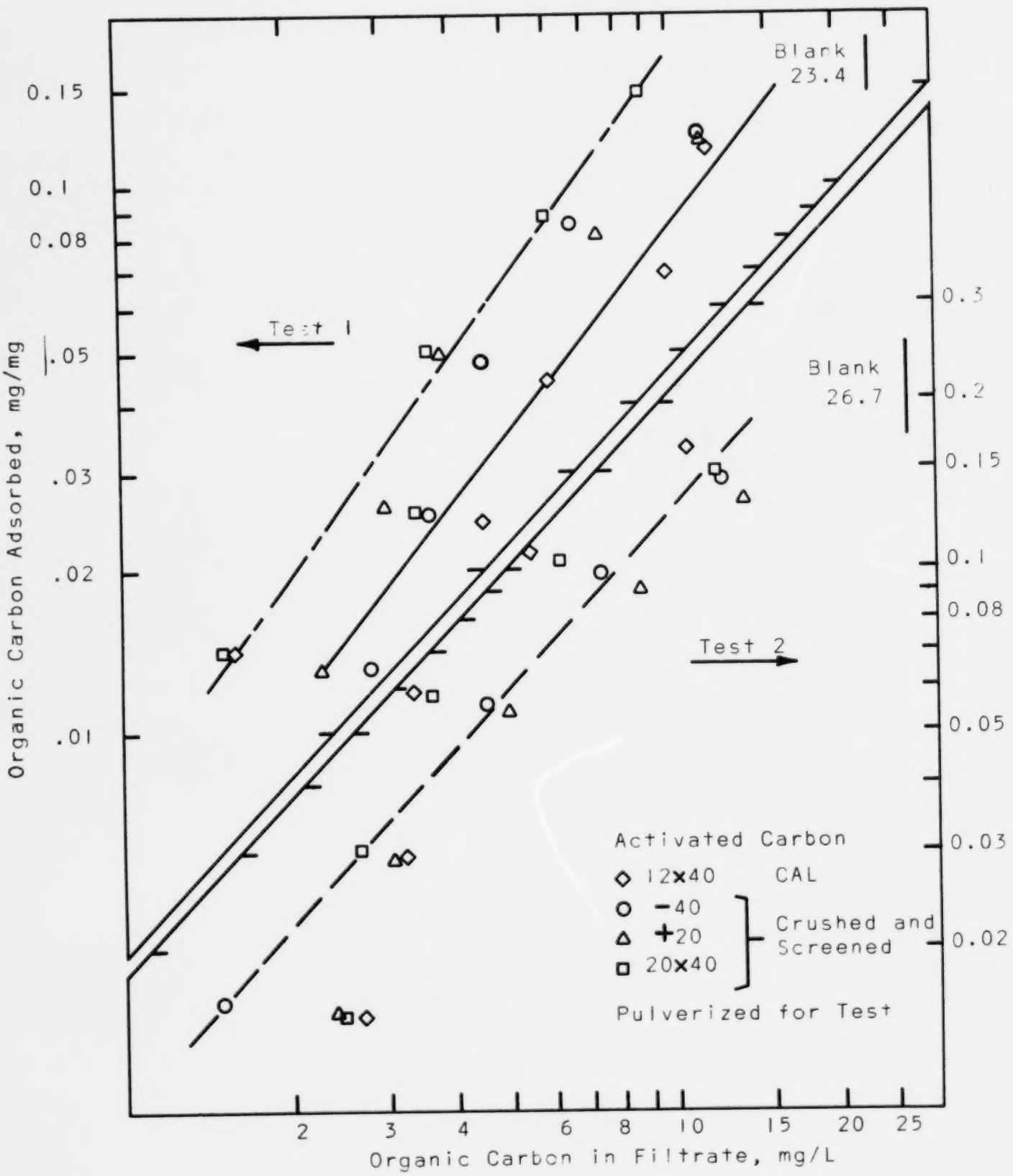



FIGURE 3. ADSORPTION ISOTHERMS FOR SECONDARY EFFLUENT ON ACTIVATED CARBON

experiments, of course, would show no differences in adsorption characteristics which might result from the physical difference of particle size, since all samples of carbon were pulverized to the same size before testing. The sole purpose of these tests was to determine whether the size fractionation operations produced fractions that exhibited significantly different activity for removal of organic carbon from secondary effluent. The only activity differences of the various particle size fractions which might have been uncovered in this particular series of experiments are those which are themselves not properties of particle size but which might result from separation according to particle size.

A similar test was carried out with unpulverized 0.1-gram samples of activated carbon of the several different particle size ranges. These samples were added to 100-ml aliquots of secondary effluent and vigorously agitated for extended periods of time. This test was conducted on two occasions to compare the 12x40 and the 20x40 fractions of the activated carbon. Because equilibrium between the carbon and the liquid is attained much more slowly with particles of these larger sizes than with the pulverized carbon, it was necessary to extend the length of the runs to about 100 hrs. The results of these experiments are shown in Table 2. Separate samples of the secondary effluent containing no activated carbon were agitated for the same period as those containing the carbon, and the concentration of organic carbon after filtration was measured at various times during this period.

The data from this series of experiments indicate little difference in the adsorption properties of the two size ranges of the activated carbon (12x40 and 20x40). The difference in the average particle size, i.e., 1.0 mm vs. 0.67 mm, is apparently not sufficient to affect either the rate of adsorption or the total amount that can be adsorbed. Very little adsorption was observed in 1 hr with either size granular carbon, and the amount of organic carbon adsorbed in 100 hr was comparable to that adsorbed by the pulverized samples after 1 hr. The samples of secondary effluent differ in the sense that the sample taken for the test on November 2 appears to contain organic material which is somewhat less readily adsorbable than the sample taken on October 25.

TABLE 2

Laboratory Adsorption Test Results for
Removal of Organic Carbon From Filtered Secondary Effluent
By Pittsburgh CAL Granular Activated Carbon

| Contact Time | Organic Carbon Concentration, mg/l | | |
|---|---|---|---|
| | BLANK | 12x40 mesh | 20x40 mesh |
| | (Results for 10/25/67) | | |
| 5 minutes | | 23.5 | 23.5 |
| 30 minutes | 28.0 | 23.0 | 22.0 |
| 1 hour | | 22.8 | 22.0 |
| 2 hours | 31.0 | 21.0 | 19.5 |
| 4 hours | | 18.0 | 17.0 |
| 24 hours | 30.0 | 11.0 | 11.0 |
| Average Blank | 29.7 | | |
| | (Results for 11/2/67) | | |
| 5 minutes | | 27.0 | 24.5 |
| 30 minutes | 26.0 | 26.0 | 23.5 |
| 1 hour | | 27.0 | 27.0 |
| 2 hours | | 23.5 | 24.0 |
| 4 hours | 30.0 | 21.8 | 17.1 |
| 24 hours | 26.8 | 13.2 | 11.0 |
| 100 hours | | 8.5 | 11.0 |
| Average Blank | 27.6 | | |
| Pulverized | | | |
| 1 hour | | 12.8 | 9.5 |

All tests in 250-ml iodine flasks with 100 ml filtered secondary effluent. Activated carbon in 0.100-gm amounts added then flask shaken for time indicated. Contents filtered through Whatman No. 42 and organic carbon determined on filtrate.

## PILOT PLANT PROGRAM

The pilot plant field program for comparative evaluation of packed-bed and expanded-bed modes of contacting activated carbon with secondary sewage effluent was divided into three principal phases. Phase I of the program involved field testing of 6-in. diameter columns of activated carbon with an expanded-bed mode of operation. These columns were constructed of Pyrex glass pipe to facilitate observation of the behavior of the expanded bed. Larger steel columns were used in later phases. The smaller size of the glass columns, coupled with their transparency, allowed greater flexibility in the test program for experimentation with other media, and in cleaning procedures. Phase II of the program was a 100-day comparative study of packed-bed and expanded-bed modes of operation using 10-in. diameter steel columns, with a total depth (settled) of carbon of 12 ft. Both unfiltered and sand-filtered secondary effluents were tested in parallel operations during Phase II. Phase III was a 90-day comparative study of packed-bed and expanded-bed (10-in. diameter, 24-ft settled depth) modes of operation with a chemically clarified and sand filtered secondary effluent.

The experimental work was conducted at the treatment plant of the Ewing-Lawrence Sewerage Treating Authority (ELSA) near Trenton, N.J. This plant serves most of the residential, commercial, and industrial areas within the two townships. The sewage is comprised of about 25% industrial waste and 75% domestic waste. A schematic diagram of the ELSA plant is given in Figure 4. The original plant, consisting of two lines (primary sedimentation, trickling filter and secondary sedimentation) went into operation in 1953 and was expanded in 1964 by addition of two larger lines and a larger chlorine detention tank. The plant is designed for an average daily flow of 9 mgd with pumping capacity of 30 mgd, the average daily flow is about 7 mgd.

Chlorinated secondary effluent for the studies was taken from the line supplying utility requirements of the sewage treatment plant. The experimental apparatus was set up on a poured concrete slab installed specifically for this project next to the ELSA return-pump building. The steel columns resting on the slab were secured to an angle-iron frame to maintain vertical position. The filter and other tanks were located on the slab and pumps, valves, and controls were installed in a 10-ft x 12-ft building constructed on the slab. Connections between columns and valves were rubber hoses through the building wall. The smaller glass columns used for the Phase I studies were set up next to the building.

Figure 5 is the pilot plant flow diagram and Figure 6 shows photographs of the installation.

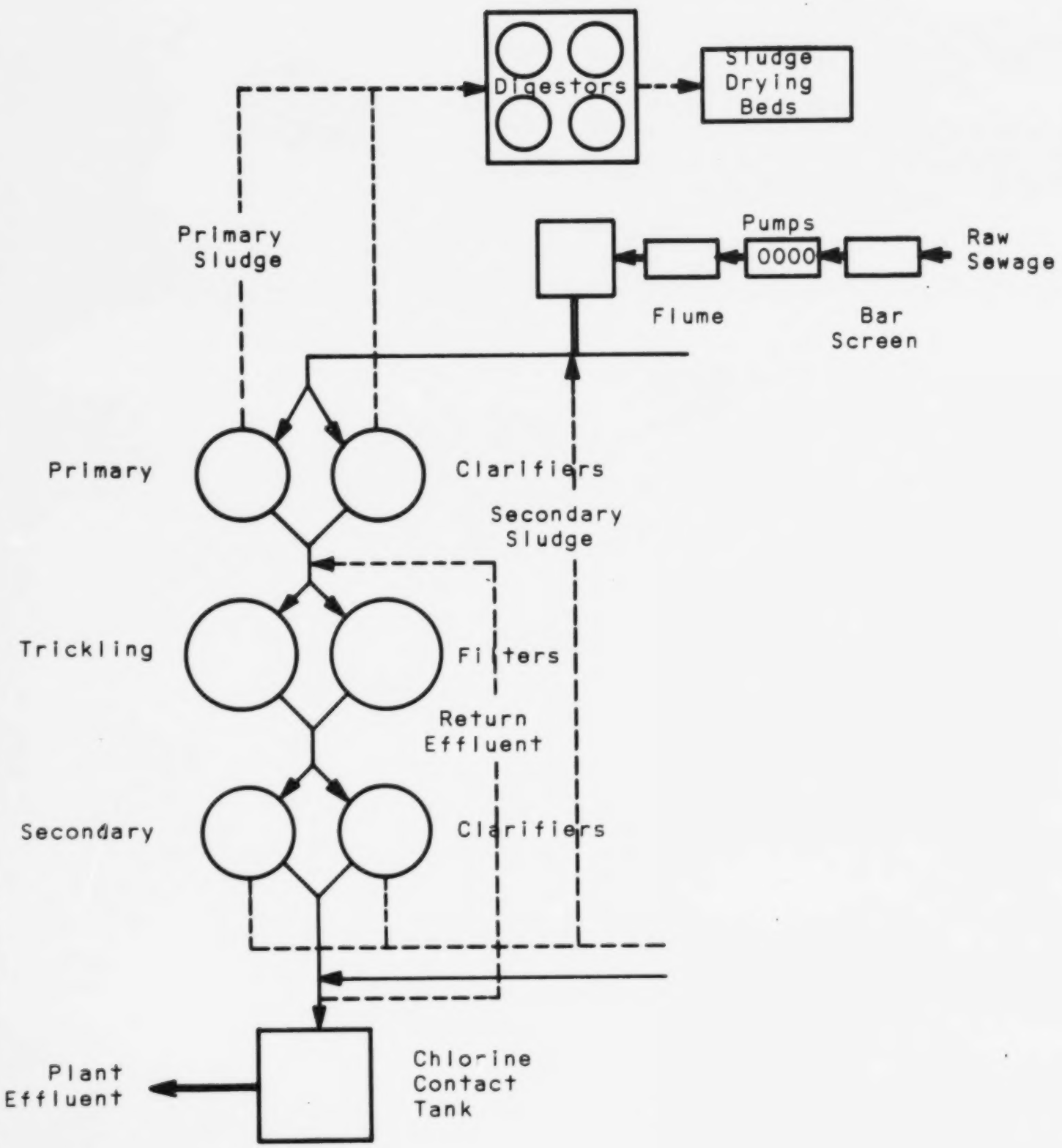



FIGURE 4. FLOW DIAGRAM EWING-LAWRENCE SEWERAGE AUTHORITY PLANT

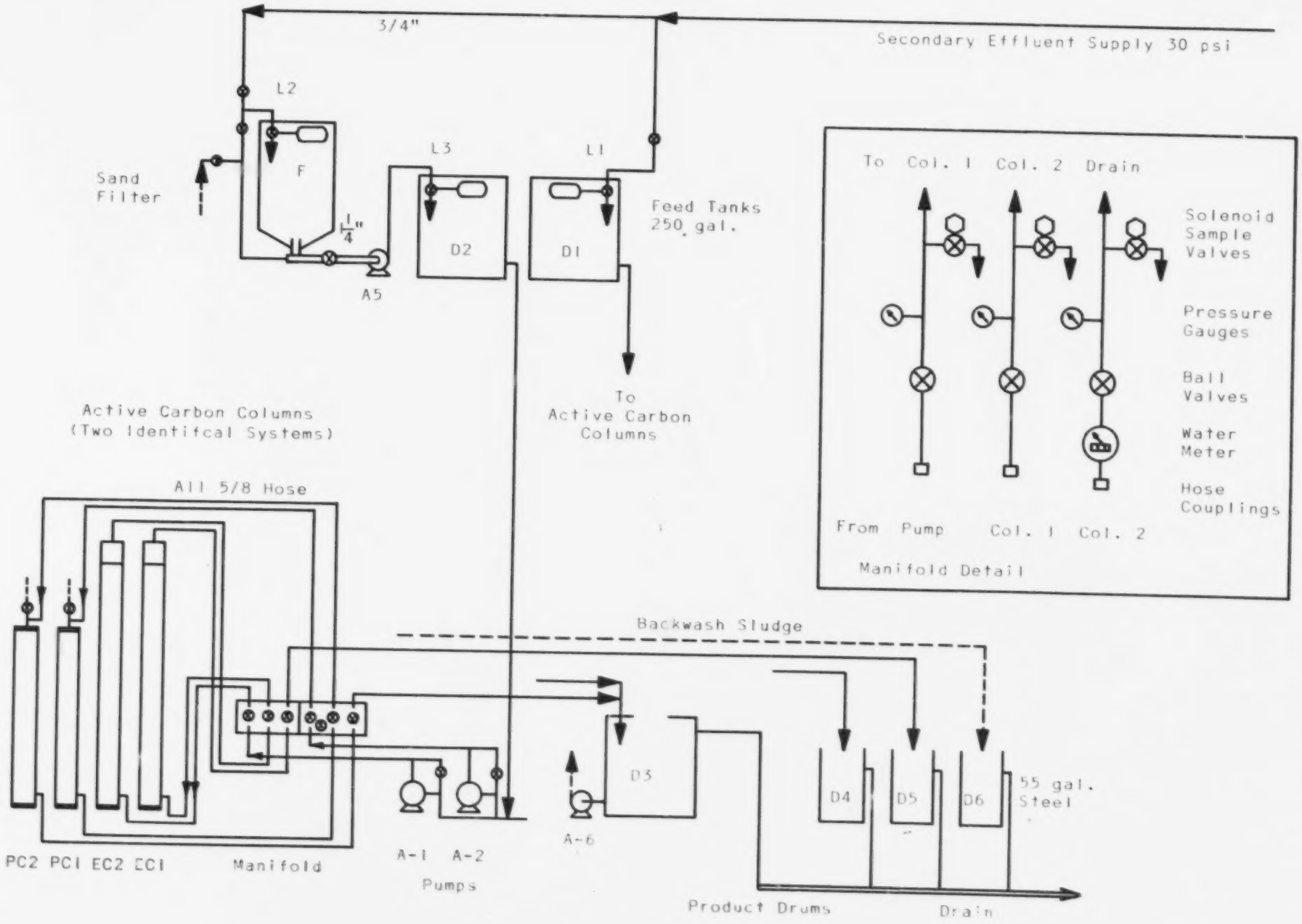
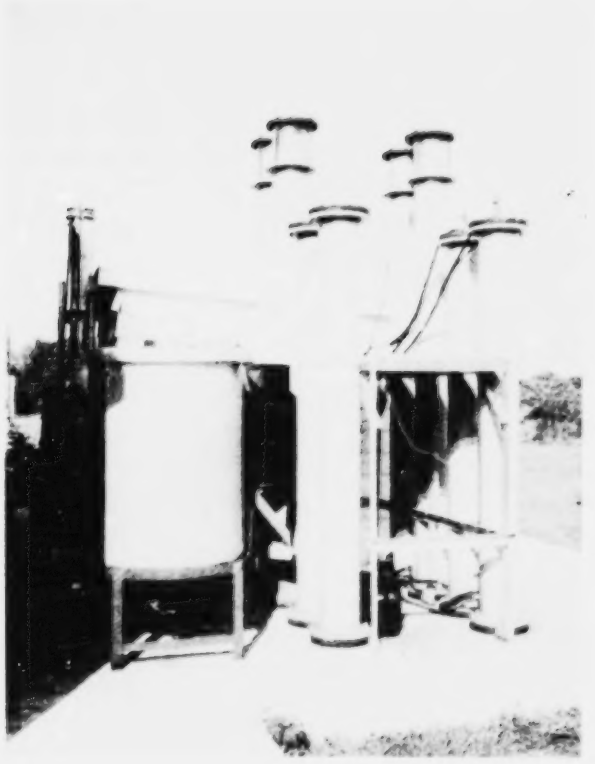
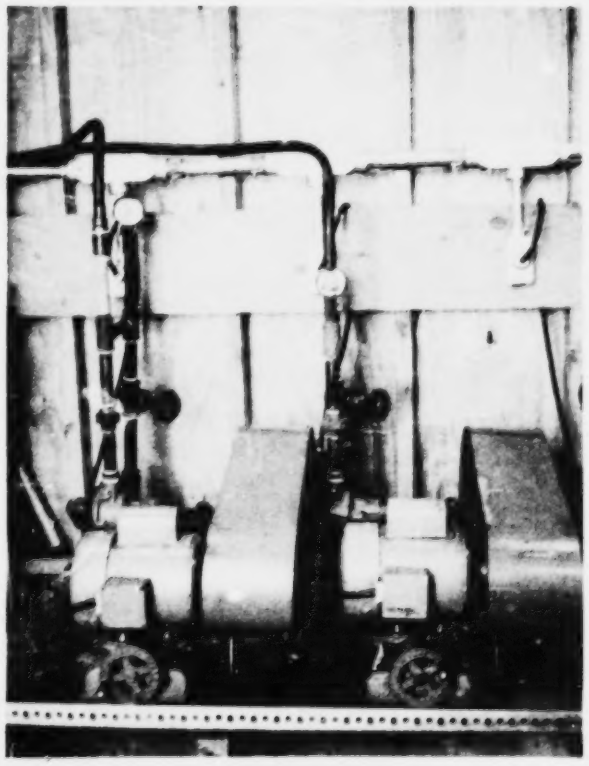



FIGURE 5. FLOW DIAGRAM OF FIELD TEST UNIT

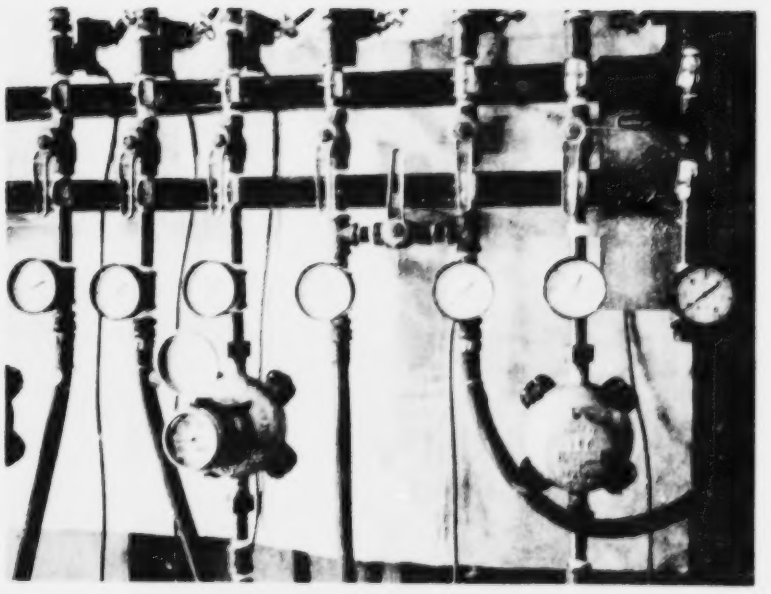
PILOT PLANT INSTALLATION



FILTER AND COLUMNS



FEED PUMPS



VALVES & METERS

FIGURE 6 PHOTOGRAPHS OF PILOT PLANT EQUIPMENT

Daily samples of the secondary effluent feed and product from the operations were taken for analysis. The pilot column systems included timer-operated solenoid sampling valves which were set to collect approximately 10 l/day in approximately 100-ml increments at 15-minute intervals. For weekend operation, the increment was decreased and the interval increased to provide a reasonable size sample for the longer period. To inhibit biological action in the organic materials in the sample, acid was added to the containers before sample collection. The composited samples were thoroughly mixed before withdrawing an aliquot for analysis in the laboratory. The product from the glass column systems was spot sampled at the time the other samples were taken.

The analyses performed on the column feed and effluent included determination of total organic carbon (TOC), soluble organic carbon (SOC), suspended solids (SS), and turbidity. Organic carbon measurements were made in a Beckman Carbonaceous analyzer by injection of an aliquot of acidified and nitrogen stripped sample. The TOC was determined directly, and the SOC determined on the filtrate from the suspended solids determination. The value for TOC gave a measure of the carbon contribution from both soluble and suspended organic materials.

Suspended solids concentration was measured by a procedure[8] which involved filtration of a portion of the sample through a membrane filter with 0.45-micron openings, which was then dried to constant weight. Prior to use, the membrane filter was washed in distilled water to remove water soluble impurities, and dried to constant tare weight with individual desiccators for each membrane.

## PILOT PROGRAM PHASE I

### Apparatus and Procedure

A 6-in. diameter glass column containing an approximately 4-ft-deep bed of 20x40 activated carbon supported on gravel was set up at the pilot plant site. Chlorinated secondary effluent was pumped through a rotameter, upward through the expanded carbon in the column, then through a meter to discharge. The flow rate was maintained at about 1 gpm, corresponding to 5 gpm/ft$^2$ of column area. The glass column was completely covered with an opaque wrapping, except during inspection, to prevent photosynthetic activity.

### Experimental Results of Adsorption Run

Data for the first test are presented in Figure 7. The experiment was interrupted after about 24 hours of operation because of poor quality of the secondary effluent resulting from a mechanical

failure in the sewage treatment plant. This condition was corrected in two days and the column test re-started and operated continuously thereafter. From Figure 7 it can be observed that, during the first five days of continuous operation, the height of the expanded bed of carbon increased from an initial 59 in. to completely fill the 9-ft glass column. The bed height observations shown in Figure 7 are plotted with breaks which represent column cleaning and restoration of the original bed height. At the beginning of the run, the height of the static carbon bed was 46 in. The initial height of 59 in. corresponds to an expansion of about 128% which is essentially the same as observed in experiments with tap water for the same temperature range. Visual observations of the carbon bed during the course of the run indicated that the relatively uniform increase in the degree of expansion was paralleled by a relatively uniform increase in the number of particles of carbon which became coated with sludge and which, as a result of decreased density, accumulated in the upper region of the expanded bed.

The carbon in the lower part of the bed was unchanged in appearance, whereas the carbon in the middle zones of the bed took on a greyish-brown color as individual particles became completely surrounded by a gelatinous coating. The top 2 in. of the bed consisted of a tan or brown flock which appeared to consist of only biological sludge particles.

At this point, the bed was cleaned in place with a water jet located at the top of the bed, followed by flushing at a high rate through a jet located at the bottom of the column. All cleaning was carried out using carbon-treated secondary effluent. It was necessary to repeat this procedure several times until the agglomerations of sludge and sludge-coated carbon in the middle of the bed were broken up and dislodged. One possible cause for the difficulty in breaking up the agglomerations near the middle of the bed was the 4-hr delay between stopping the flow to the column and the beginning of the cleaning procedure. During this period of inactivity, the bed relaxed, and, under settling forces, the sludge-laden carbon compacted; the static height of the settled bed was not much greater than when no sludge was present. This problem was minimized in subsequent cleanings by avoiding delays. After cleaning, the bed showed the same general appearance and original settled depth, although it still contained a few small sludge and sludge-coated carbon agglomerates.

From organic carbon data shown in Figure 7, it is readily evident that 4 ft of carbon was not adequate for effective removal of organic contaminants from the secondary effluent at the flow rate utilized in these experiments. Variations in removal can be noted which do not appear to be related to the build-up of sludge in the carbon bed. The variable width of the band between the TOC of the feed and product waters for a relatively constant flow rate indicates that there were variations in the extent of

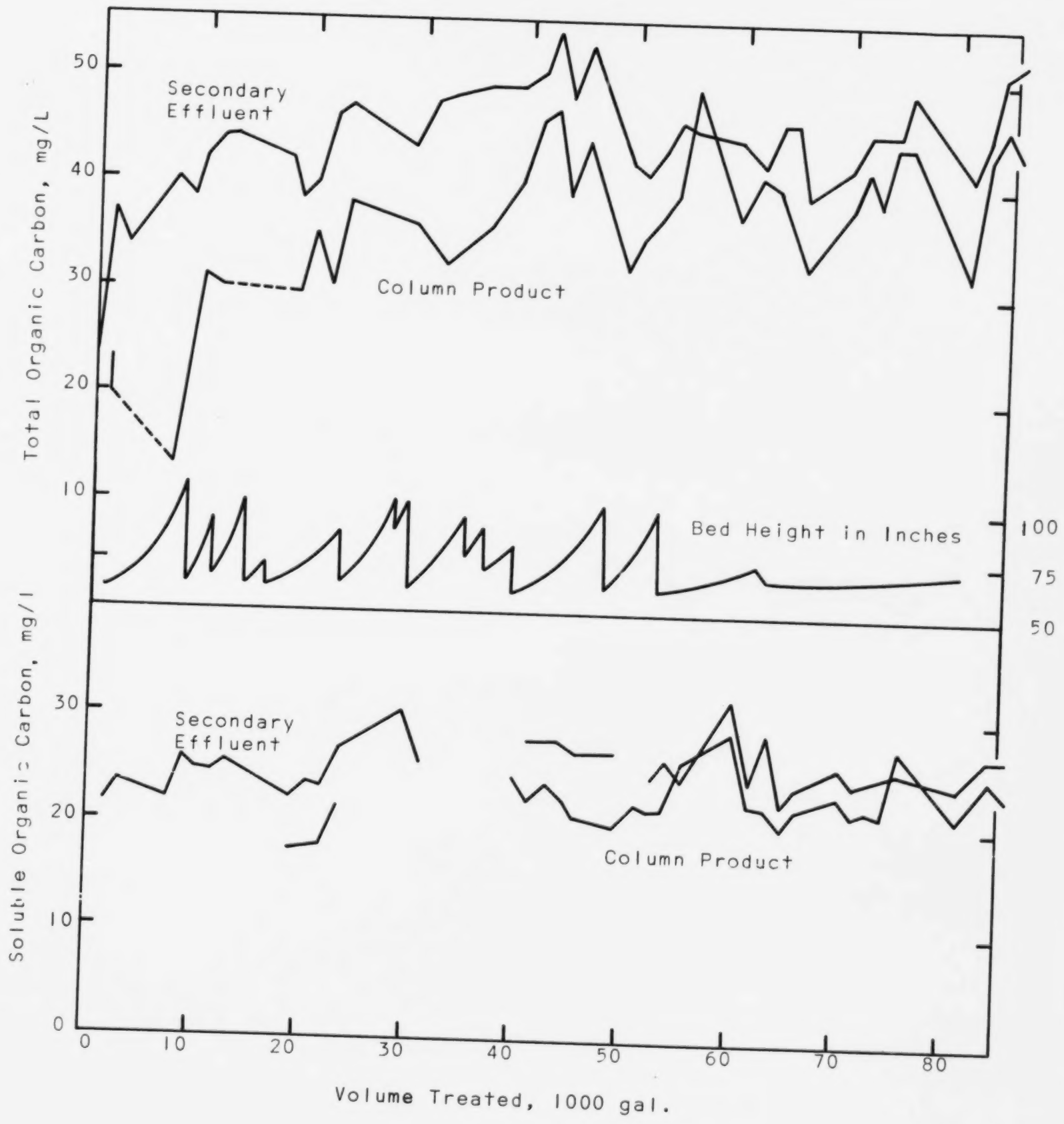



FIGURE 7. TREATMENT OF SECONDARY EFFLUENT WITH ACTIVATED CARBON IN 6-IN. DIAMETER UPFLOW COLUMNS

removal of TOC with time, suggesting differences in the characteristics of the organic substances comprising the TOC.

Data on TOC removed during the course of a second 2-month test run in the 6-in. glass column indicate that about 0.1 to 0.2 lb per day of organic carbon was removed by about 20 lb of activated carbon during its active removal phases under the experimental conditions. As in the first 2-month run, organic removal varied from day to day suggesting differences in composition of the wastewater.

Very little removal of organic carbon was observed during the latter phases of operation of the glass column, and at the same time the need for cleaning the column because of excessive expansion of the bed diminished. The biological growth on the particles of carbon which caused increased expansion of the bed decreased as the carbon became exhausted. There are several possible explanations for the decline in biological growth as the sorptive capacity of the activated carbon is being depleted. Organic food and nutrients were continuously supplied in the influent to the carbon columns, as was dissolved oxygen. Apparently, when extensive adsorption of organic material led to saturation of the carbon surfaces, the possibility of sufficient quantities of essential elements being in the vicinity of the surface at the concentrations needed for prolific growth was greatly decreased. The observation that biological growth on the activated carbon appeared to be a function of the organic removal activity of the carbon should not be misconstrued to imply that removal activity was dependent upon or even a function of biological growth. As the biological films developed, the rates of TOC removal established in their absence by the clean carbon remained virtually unchanged.

Inert Media Test

To further examine the role of the biological growths which accumulated on the activated carbon during the first 2-month run with the expanded bed in the glass column, two additional experimental runs were carried out. Two identical 6-in. diameter glass columns were constructed. One was filled to a depth of 4 ft with 20x40 activated carbon, and the other with a like charge of 20x40 bituminous coal. The coal was selected and prepared in such manner that its density and particle shape and size were very nearly identical to those of the carbon. Thus, while the coal should have little or no adsorptive capacity for organic contaminants, its physical and hydraulic behavior in the experimental column tests would be the same as for the activated carbon. These two parallel column tests were carried out with the same flow rate, quantity of carbon or coal, and system geometry as used in the previous glass-column tests. However, during the period of this run, the water temperature was lower, averaging about 5°C. Additionally, the average concentration of TOC in the feed was higher than for the earlier runs. Data from these parallel runs are plotted in Figure 8.

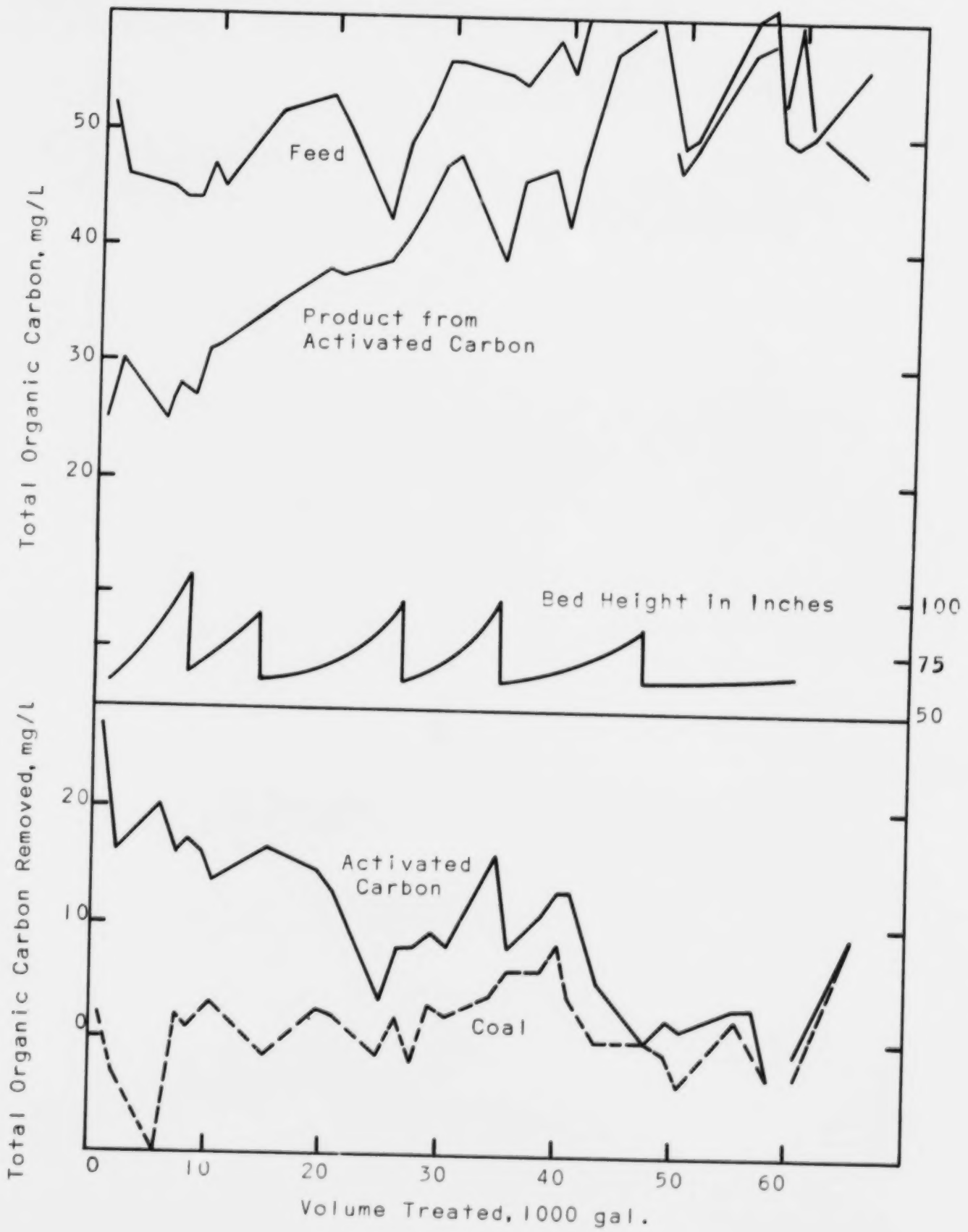



FIGURE 8. TREATMENT OF SECONDARY EFFLUENT IN 6-IN. DIAMETER UPFLOW COLUMNS CONTAINING ACTIVATED CARBON OR COAL

The results obtained with the column containing the activated carbon were similar to those observed previously. The bed of coal, however, removed little TOC, and little biological coating of the particles occurred. A small amount of sludge floc formed above the bed of coal. During the latter stages of these runs, coal particles were observed to be transported out of the bed by gas bubbles which apparently formed within the bed. This behavior was not observed to any extent in the bed of activated carbon operating on the same secondary effluent at the same time. There was no evidence of septic conditions in either the coal or activated carbon beds.

The results of the parallel experiments with activated carbon and "inactive" bituminous coal do illustrate and confirm the earlier observations that the development of the biological slimes around individual carbon particles in an expanded bed is related to the sorptive activity of that carbon.

Cleaning Operations

The glass column was useful for making a search for effective methods for in-place cleaning of the sludge-coated carbon. The first attempts to clean the carbon beds, using jets of water at the surface and bottom of the bed were effective only in limited regions of the bed. The next cleaning method tested consisted of inserting a motor-driven 3-in. turbine propellor into the column to a depth of about 3 ft below the top of the expanded bed and alternately stirring (60 rpm) and flushing with water. This was found to be a rather effective method for dislodging sludge from the carbon particles in the very limited part of the column in the immediate vicinity and above the propellor blades, but the procedure did not break up the agglomerates in the middle of the bed, where neither the bottom jet nor the stirring provided adequate scrubbing or scouring.

A third cleaning technique, involving a high-pressure air jet at the end of a copper tube which was moved continuously about in the expanded bed from the top to the bottom of the column, was found to be the most effective. This procedure required considerably less time; usually two cycles of air scouring followed by back flushing at high rate thoroughly cleaned the bed. Subsequently, the compressed air was introduced to the column in the influent feed line for simpler and more rapid cleaning. This procedure also served to remove any sludge that had accumulated in the gravel layer surrounding the distributor.

## PILOT PROGRAM PHASE II

The second phase of the pilot program called for long-term comparative studies of packed-bed and expanded-bed columns for contacting activated carbon with secondary effluent. Treatment was carried out in four separate experimental systems to permit comparison of the two different contacting methods both with and without pretreatment of the secondary effluent by simple sand filtration.

## Apparatus and Procedure

The four carbon-contacting systems consisted of vertical columns constructed of 10-in. diameter steel pipe* connected as shown schematically in Figure 9. Each column, as shown in Figure 10, was charged with 85 lb of activated carbon, a quantity sufficient to provide a 6-ft-deep bed. The carbon was supported on a 6-in. layer of gravel and coarse sand over a 5 in. cone shaped distributor similar to that used in the glass columns. The commercial 12x40 carbon was used in the packed beds; 20x40 carbon was used in the expanded beds. The smaller size carbon in the expanded beds was used to attempt to take advantage of the potentially higher adsorption rate. The columns designed for packed-bed operation were 9 ft tall to allow for a backwashing and disengaging zone, while those designed for expanded-bed operation were 12 ft tall to provide sufficient space for bed expansion during operation. The top 1-ft section of each expanded-bed system consisted of a transparent pipe to permit observation. Two columns were connected in series to provide a 12-ft total settled depth of activated carbon for each system. This depth of carbon was chosen because studies by others indicated 12 ft of carbon would be sufficient to provide a significant degree of organic contaminant removal. A very high degree of removal would require more carbon and was not considered necessary for this phase of the work.

Each of the four systems being compared was fed by a separate constant-displacement pump. The pumps were driven by electric motors through variable speed drives to provide for adjustment of flow rate through the system. Lines to and between the columns consisted of 5/8-in. inside diameter rubber hose. All flow controls, including in-line valves, pressure gauges, flow meters, and solenoid sampling valves, were mounted on one central operating panel in order to facilitate operation and minimize operator errors.

Secondary effluent was fed directly to two of the four systems (one of the packed beds and one of the expanded beds) and filtered secondary effluent was fed to the other two systems. All systems were operated at a flow rate of 5 gpm/ft$^2$ of adsorber cross-section area, or about 2.72 gpm for the 10-in. columns.

Filtration of the secondary effluent was accomplished in a 38-in. diameter cylindrical tank containing a 9-in. layer of anthracite coal (effective size 0.59 mm) on a 9-in. bed of filter sand (effective size 0.62 mm). The filter sand in turn was supported on a coarse sand and gravel base over a pipe-grid distributor. A constant head of effluent was maintained above the filter by means of a float-controlled valve in the line which

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*The interior surfaces of the pipe were coated with 3 coats of Sherwin Williams water tank paint.

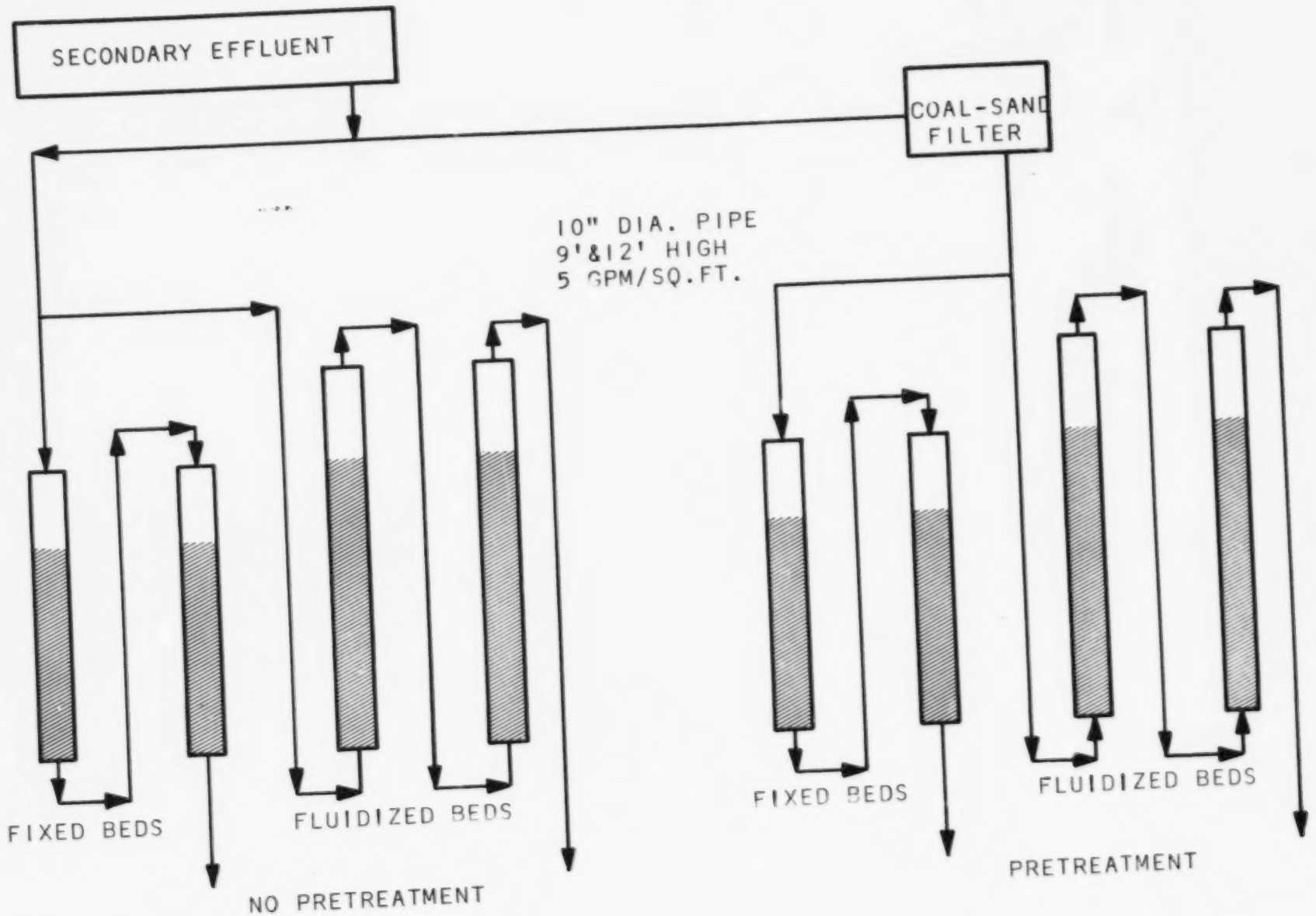


FIGURE 9. TREATMENT SCHEME

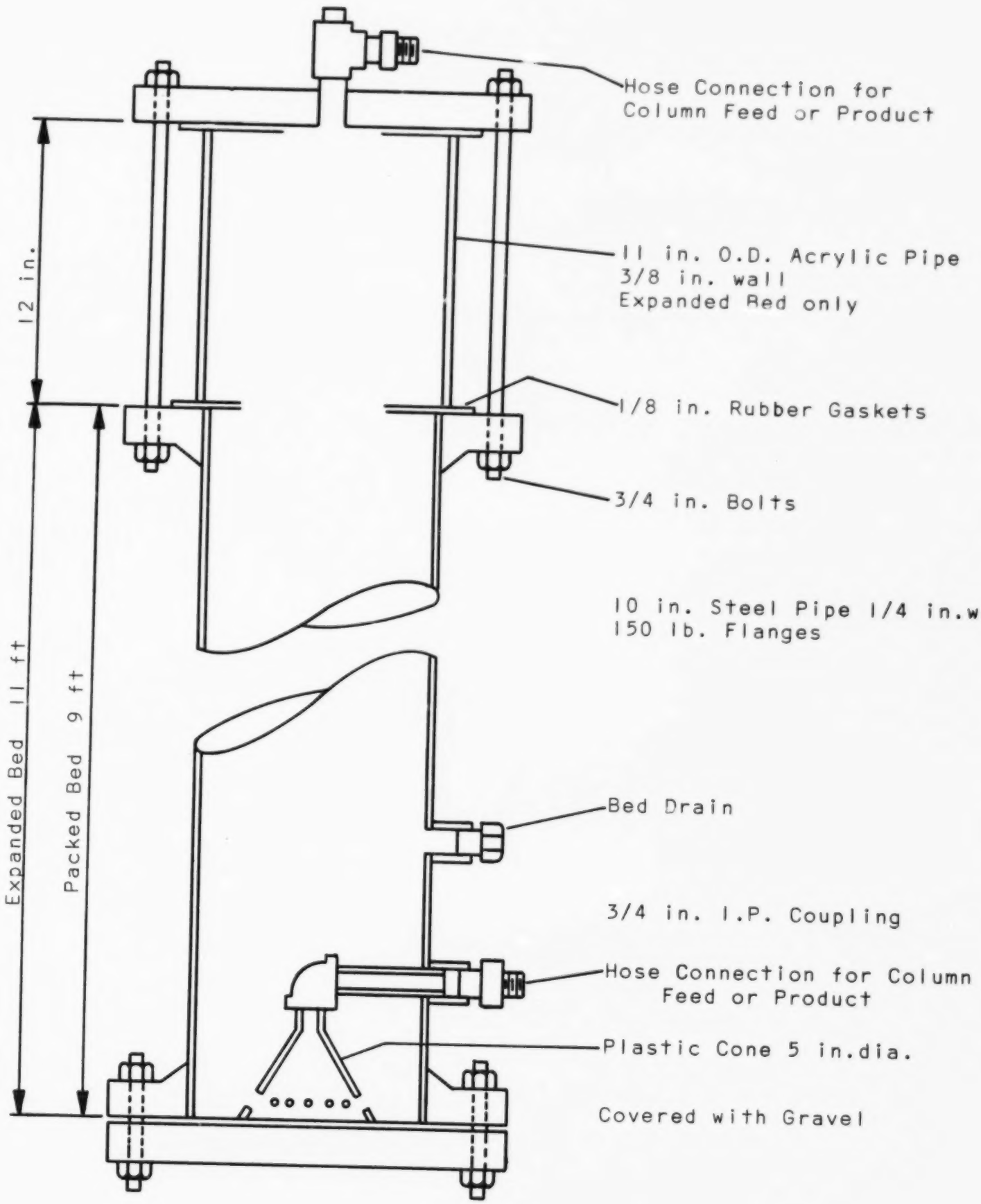


FIGURE 10. PILOT ADSORBER COLUMN DETAIL

discharged secondary effluent to the filter. The filtrate was pumped from the filter through the pipe-grid distributor by a centrifugal pump and delivered to a holding reservoir from which feed was pumped to the adsorbers.

The filter was operated at a rate of about 5.5 gpm to provide feed for two of the column systems; this rate corresponds to about 0.75 gpm/ft$^2$ of filter bed surface. Cleaning and backwashing of the filter, which was required about twice each week, was accomplished by injection of compressed air and water through the distributor. Although the sand filter consistently removed large suspended-solids particles, it did not remove the small particles that constituted most of the turbidity. As a result, there was little change in the physical appearance of the sewage. The solids which were dislodged from the filter during backwashing had the appearance of activated sludge; a dense suspension of tan or light brown particles which settled quite rapidly.

The activated-carbon-column systems were operated continuously at 5 gpm/ft$^2$ by appropriate hand adjustment of the pumping rate, the flow being measured continuously with water meters. Interruptions in operation occurred only when the columns were being cleaned, or when the pretreatment system was being serviced. A packed column was cleaned whenever the pressure drop across that column increased to a value of approximately 15 psi from an initial pressure drop of 2 or 3 psi. Because there was no measurable increase in head loss across the expanded beds during operation, the need for cleaning was based on the increase in expansion caused by the build-up of biological films on the carbon particles, as discussed earlier under Phase I. For the expanded beds, cleaning was carried out whenever the top of the bed appeared in the transparent section at the top of each column.

The most effective procedure for cleaning the 10 in. activated-carbon columns was the injection of compressed air into the bottom of the bed after drawing down the water level in the column by about 1 ft. This procedure was followed by back flushing of the bed with water to remove the solids dislodged during the air scouring. The injections of compressed air provided the vigorous scrubbing action between particles needed to dislodge solids throughout the entire depth of the bed. After air agitation, the sludge could be floated away with a gentle backwash of water. Examination of the carbon on removal from the packed columns indicated that this procedure did not cause undue particle size classification in the bed. Details of the analyses of spent carbons are given in a subsequent section.

## Experimental Results and Discussion

In the 100-day continuous operation of the four different adsorption systems, each system treated between 350,000 and 370,000 gal. of wastewater. Because the packed beds required more frequent cleaning, the volume treated by these beds was less than

the volume treated by the expanded beds. Differences in cleaning requirements for the packed-bed and expanded-bed adsorbers were significant. The first of the two expanded beds operating on unfiltered feed was cleaned only 4 times and did not require cleaning during the last 40 days of operation. The second bed in this pair was cleaned 13 times in the 100 days. The two expanded beds operating on filtered feed were cleaned 10 and 6 times, respectively. Cleaning of packed beds was required more frequently, as dictated by increases in pressure drop. The packed beds on unfiltered feed were cleaned 48 and 26 times, respectively, and the packed beds operating on filtered feed were cleaned 28 and 16 times, respectively.

The observed pressures for the packed-bed system operating on unfiltered feed are plotted in Figure 11. The total pressure drop for both beds (12 ft of carbon ) in the system was 12-14 psig when the beds were clean. The pressure drop usually increased at about 0.25 psi per hour, but on several occasions the rate of increase was greater.

Plots of TOC and SOC as a function of volume of wastewater treated are presented for the four systems in Figure 12 through 19. These plots illustrate the pattern of removal of both total and soluble organic carbon for the total 12-ft depth of each of the four different systems, as well as the pattern for TOC removal at the 6-ft depth in each system. Values for organic carbon in the respective feed solutions are plotted on each figure to provide a base reference. The bands between the feed and effluent lines, which represent the organic carbon removed in each stage of treatment, converge in a similar fashion for each of the four systems. As expected, changes in the quality of the secondary effluent fed to the adsorbers are reflected in the effluent from these systems. The gradual decline in organic carbon removal with increased volume treated is evident. This decline is shown more clearly in Figure 20. The marked daily fluctuations in percent of removal shown in this figure may be attributable in large part to daily changes in the nature of the organic components represented by the TOC and SOC values, as well as in the total concentrations of these components.

The cumulative amounts of total and soluble organic carbon applied to and removed by the activated carbon columns are plotted in Figure 21 and 22 and summarized in Table 3. In the plots, the slope of each line represents the efficiency of organic carbon removal. The unit loading of TOC or SOC on the carbon in any system at any point can be calculated by dividing the value read from the ordinate by 170, since each of the four systems contained a total of 170 pounds of activated carbon, half in each column.

Figure 21 and Table 3 show that, for both the filtered and unfiltered feeds, a slightly larger amount of TOC was removed by the packed beds than by the corresponding expanded beds. The

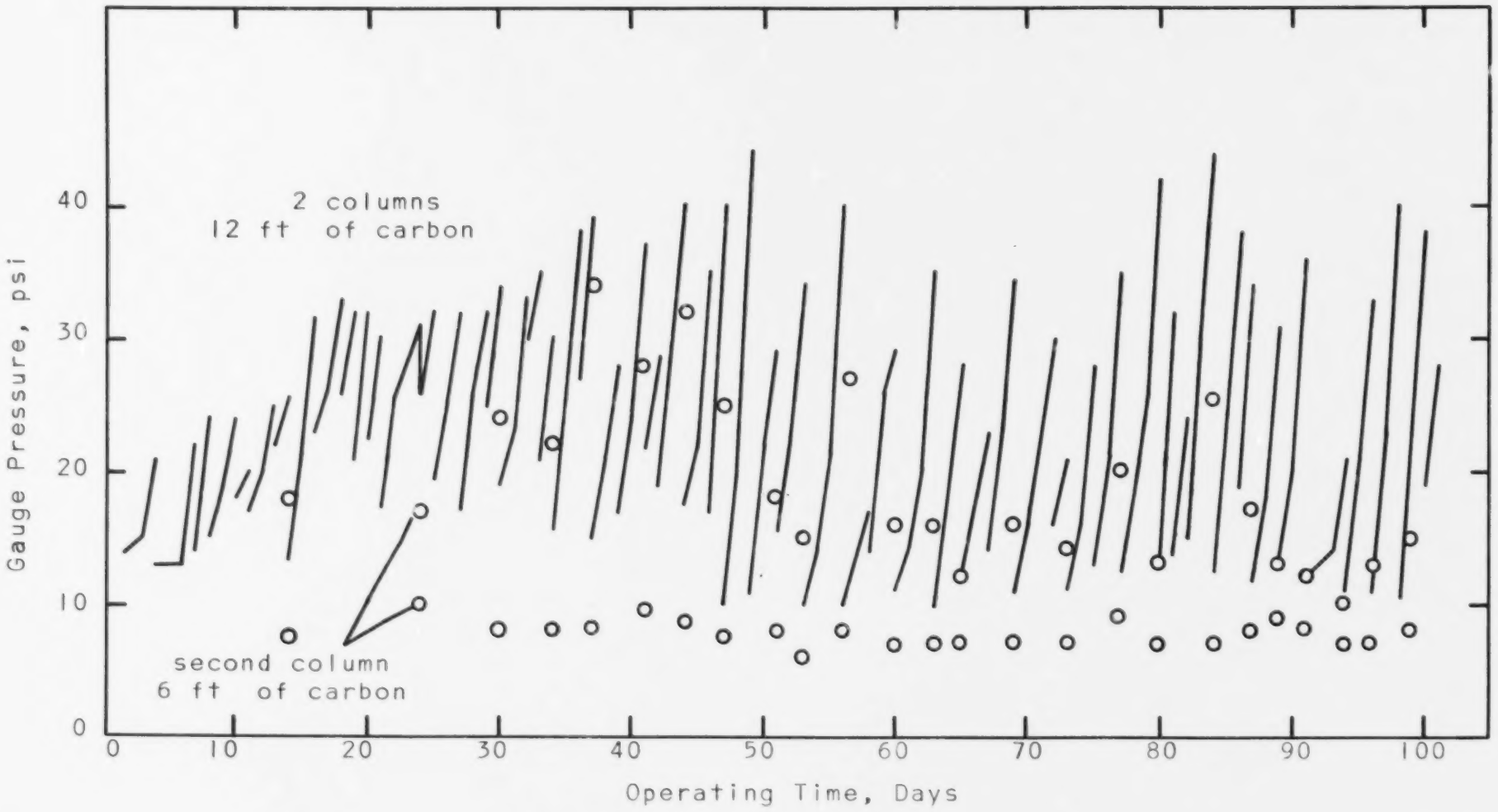


FIGURE 11. PRESSURE IN PACKED BED OF ACTIVATED CARBON DURING TREATMENT OF SECONDARY EFFLUENT

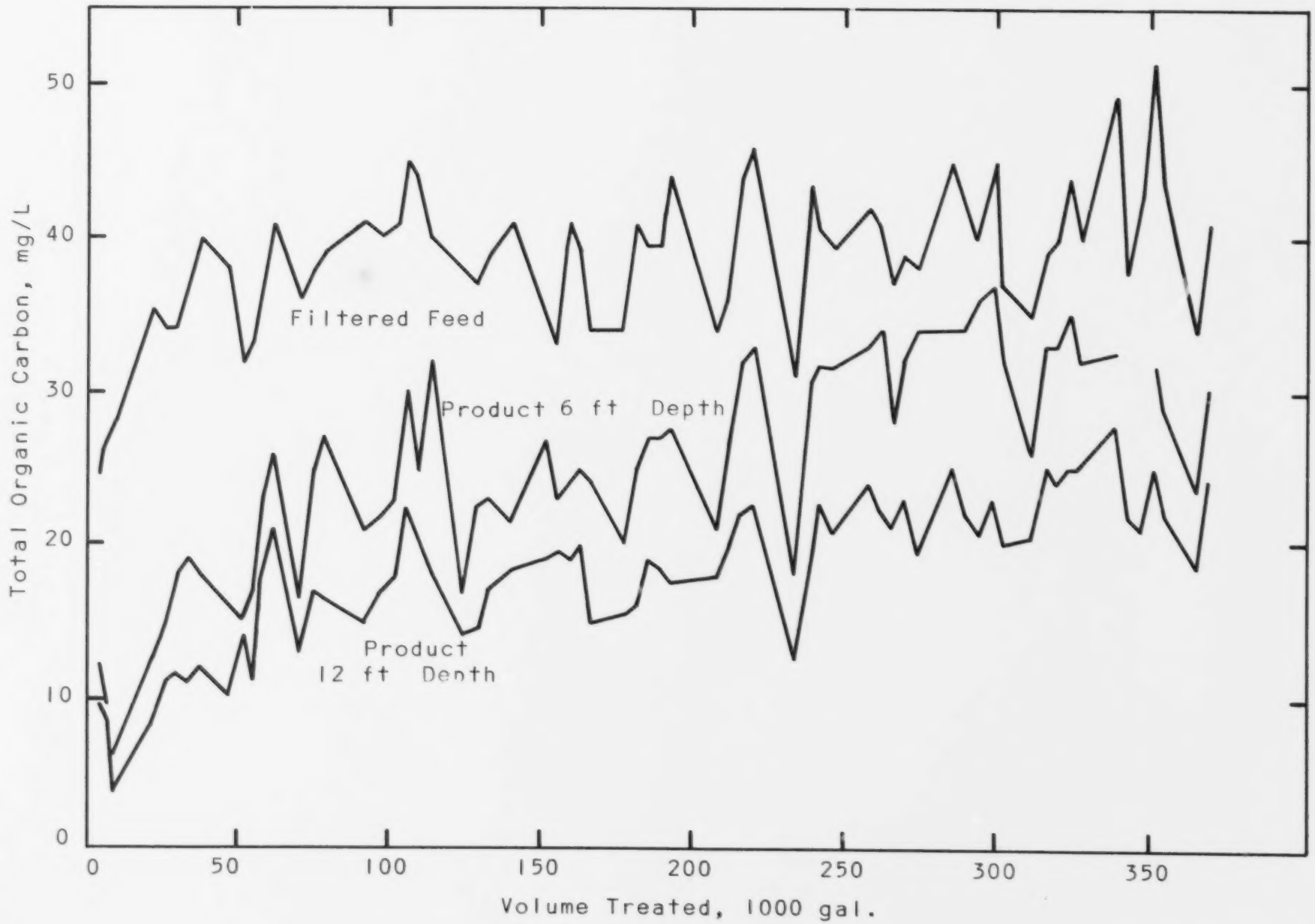


FIGURE 12. TOTAL ORGANIC REMOVAL FROM FILTERED SECONDARY EFFLUENT IN PACKED BEDS OF ACTIVATED CARBON

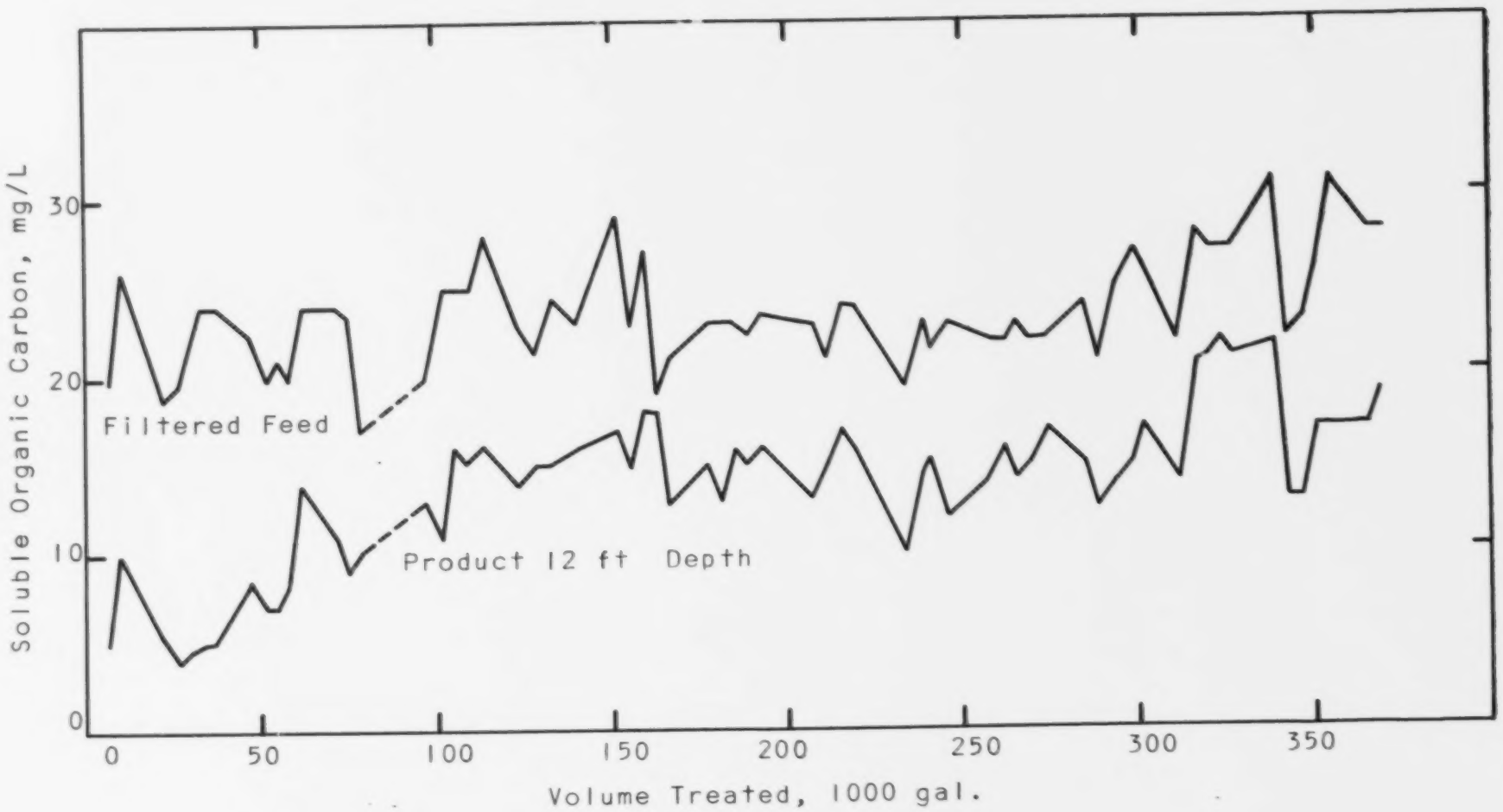


FIGURE 13. SOLUBLE ORGANIC REMOVAL FROM FILTERED SECONDARY EFFLUENT IN PACKED BEDS OF ACTIVATED CARBON

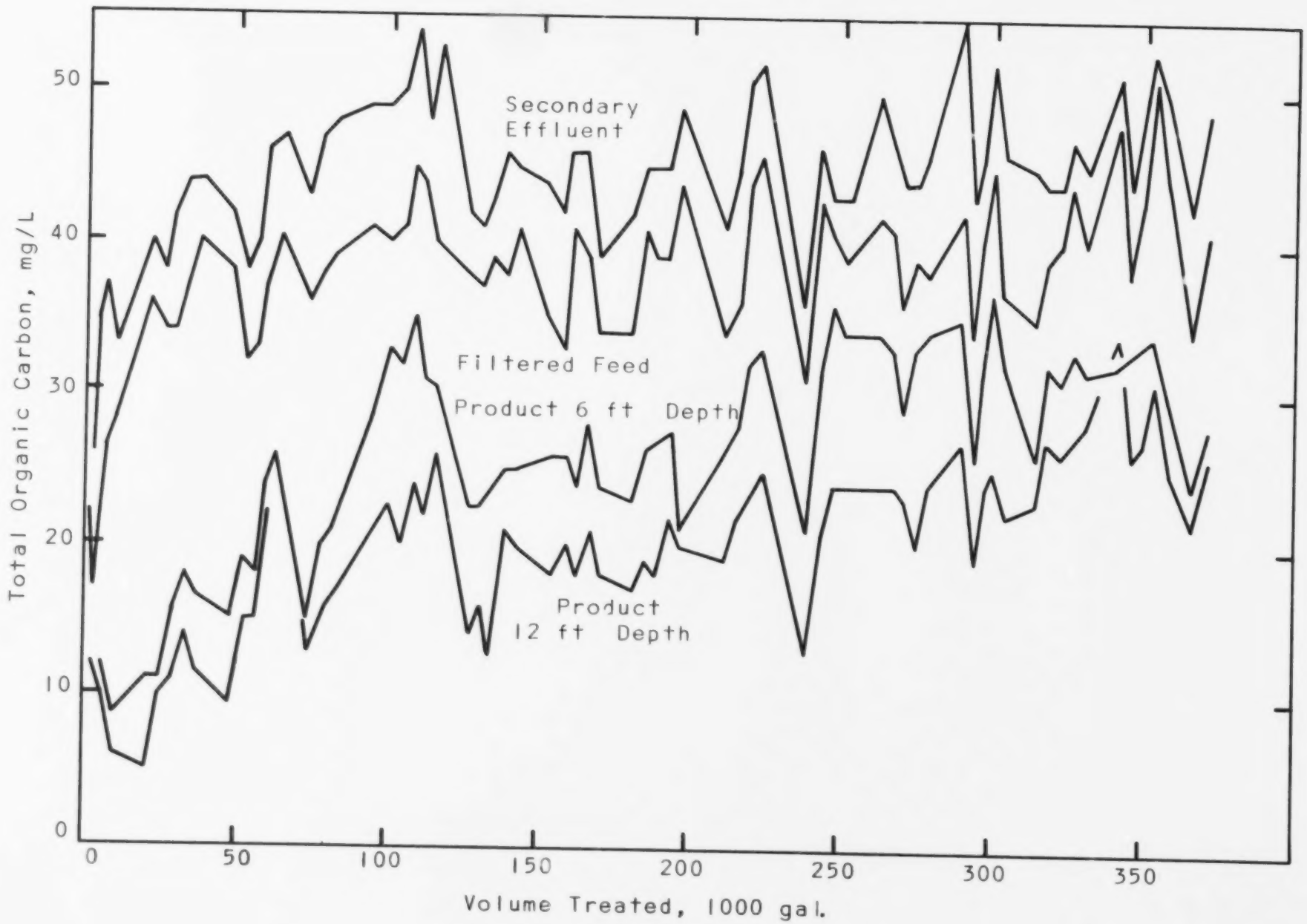


FIGURE 14. TOTAL ORGANIC REMOVAL FROM FILTERED SECONDARY EFFLUENT IN EXPANDED BEDS OF ACTIVATED CARBON

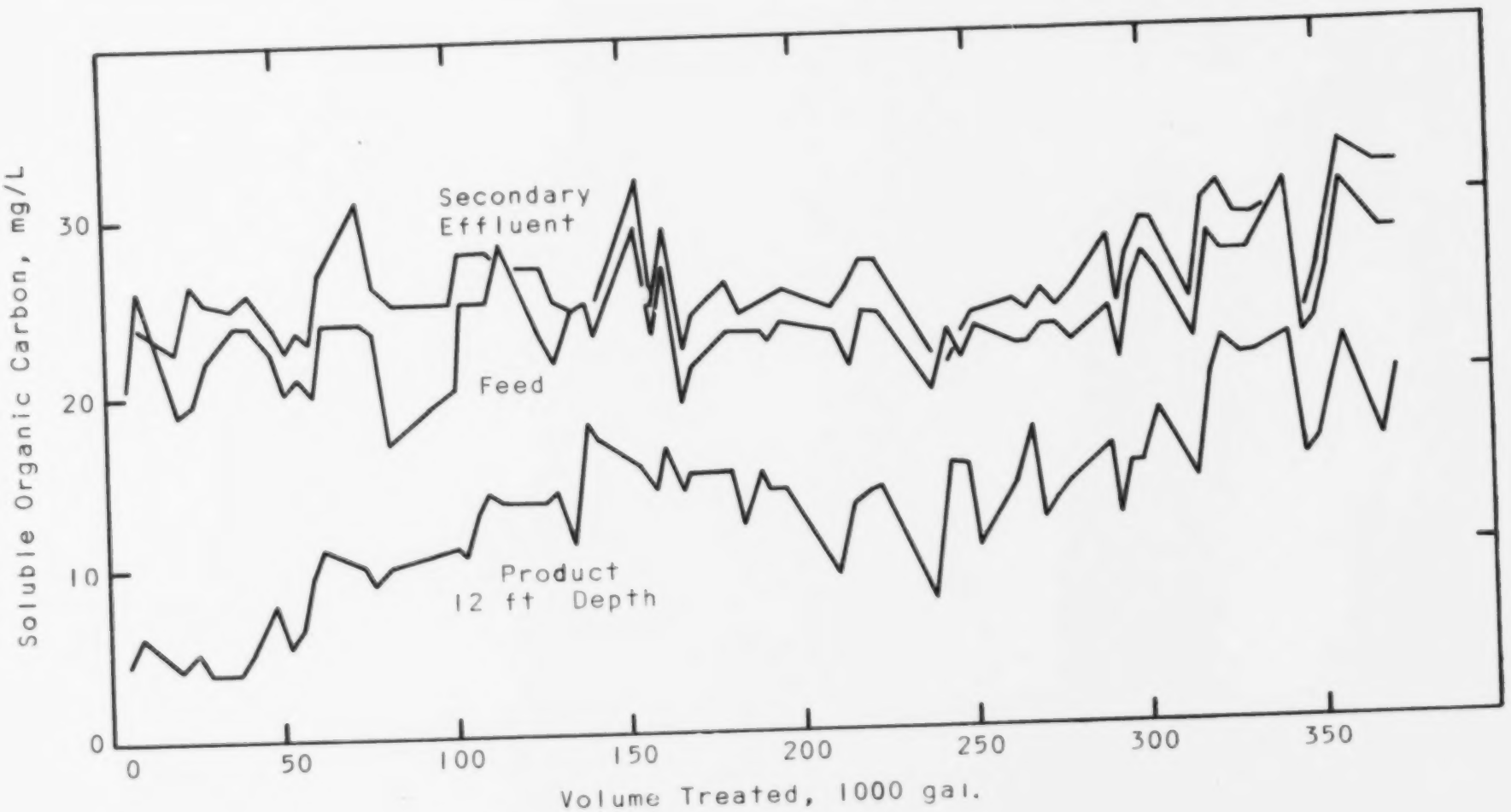


FIGURE 15. SOLUBLE ORGANIC REMOVAL FROM FILTERED SECONDARY EFFLUENT IN EXPANDED BEDS OF ACTIVATED CARBON

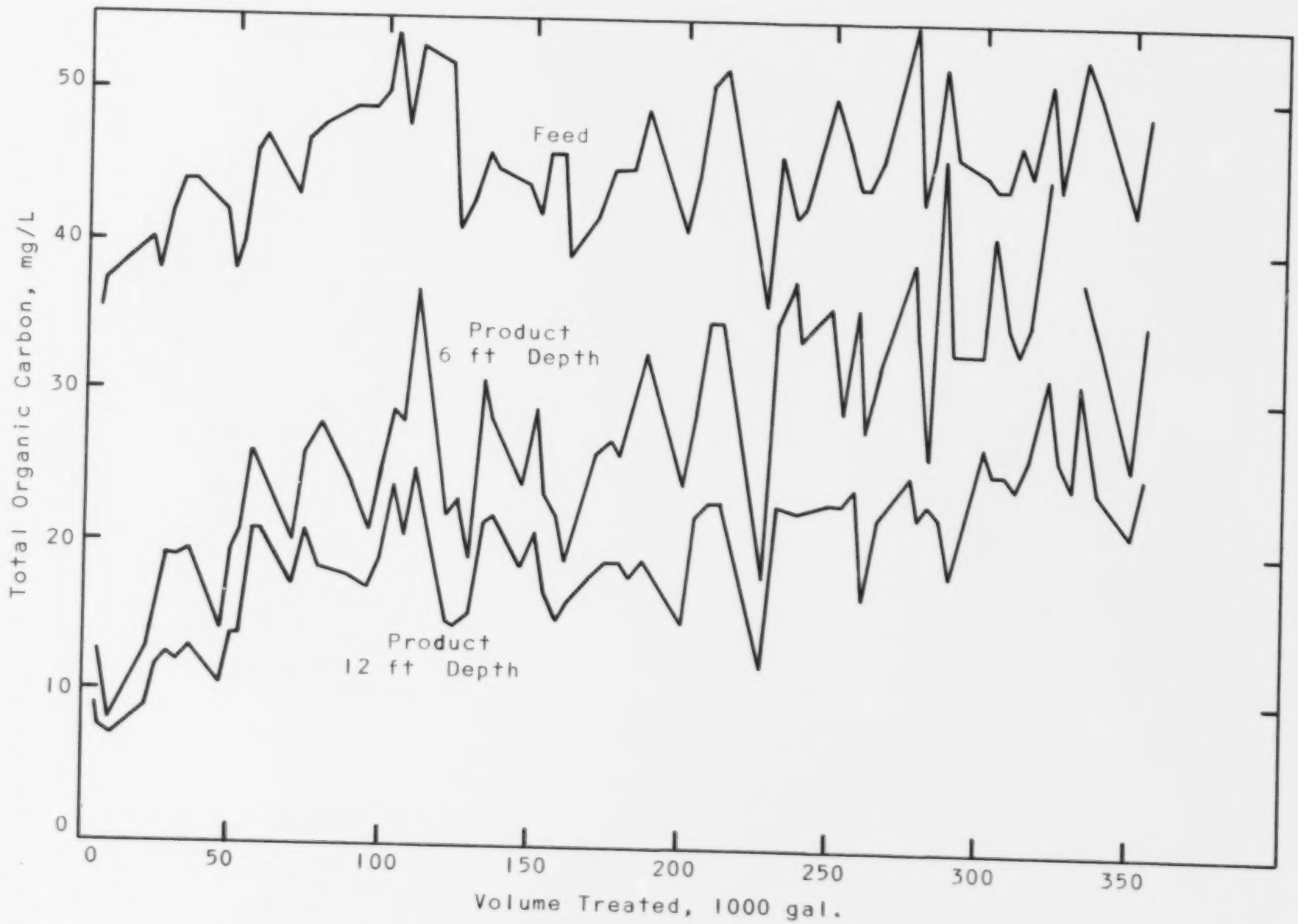


FIGURE 16. TOTAL ORGANIC REMOVAL FROM SECONDARY EFFLUENT IN PACKED BEDS OF ACTIVATED CARBON

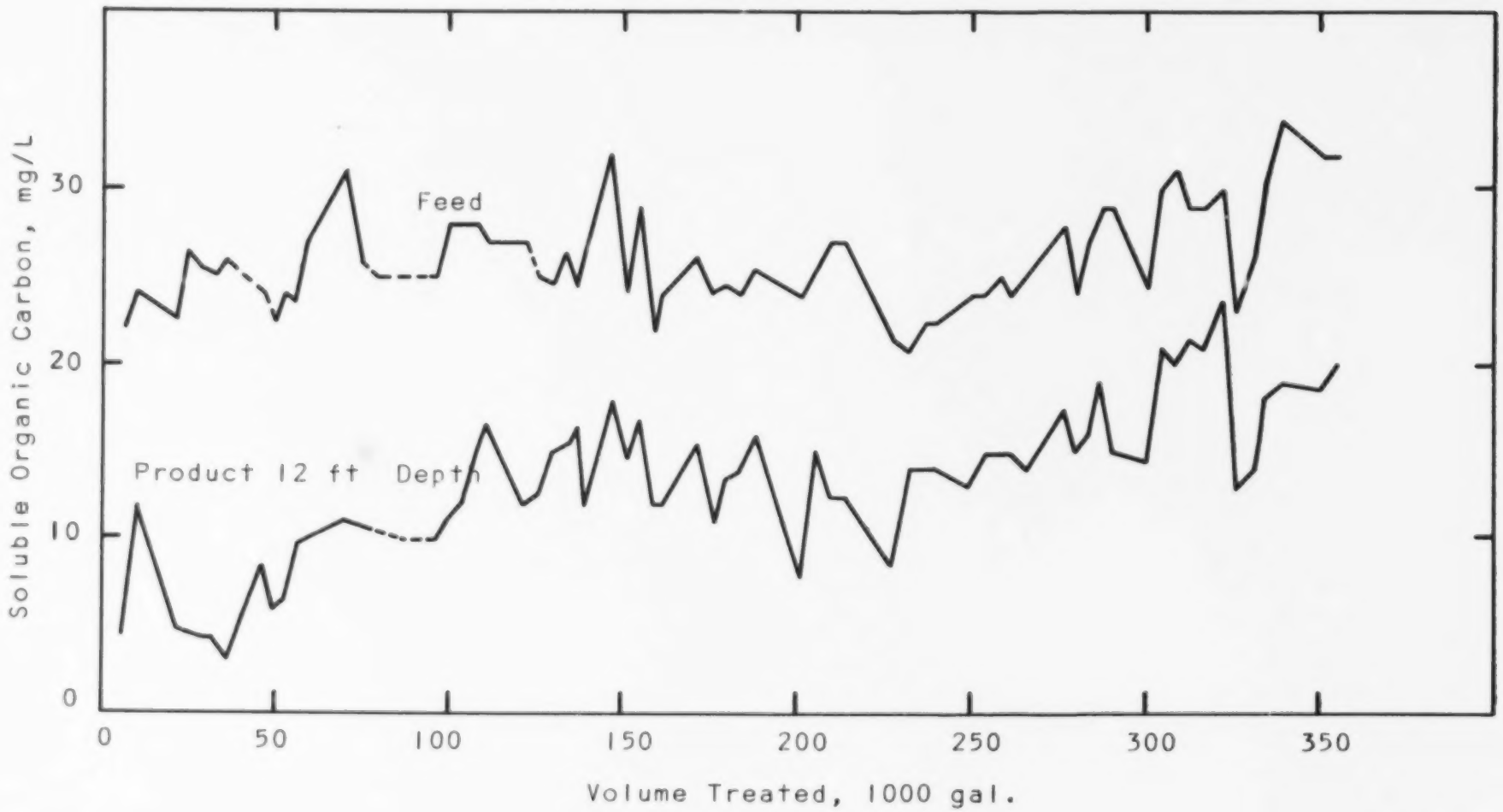


FIGURE 17. SOLUBLE ORGANIC REMOVAL FROM SECONDARY EFFLUENT IN PACKED BEDS OF ACTIVATED CARBON

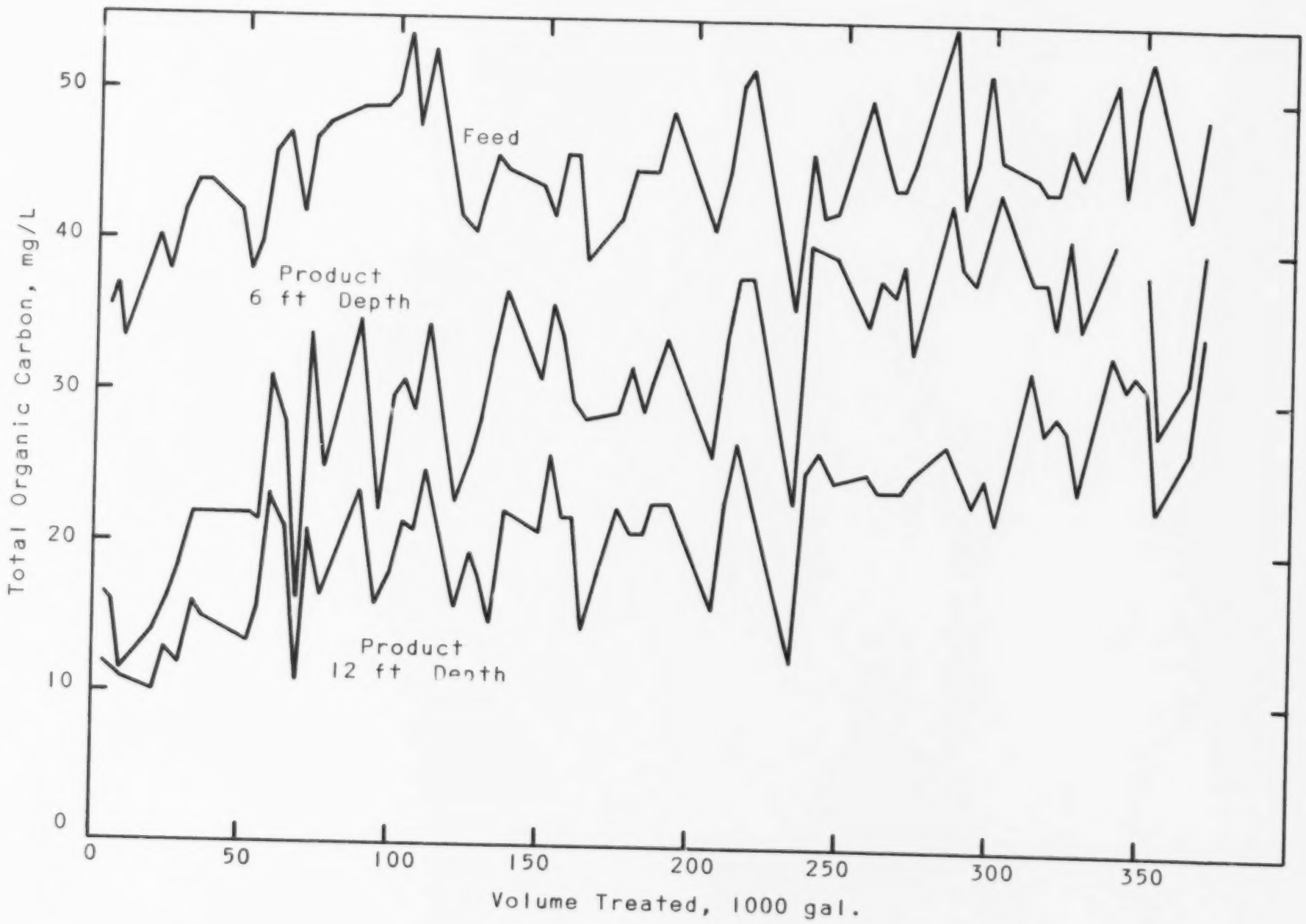


FIGURE 18. TOTAL ORGANIC REMOVAL FROM SECONDARY EFFLUENT IN EXPANDED BEDS OF ACTIVATED CARBON

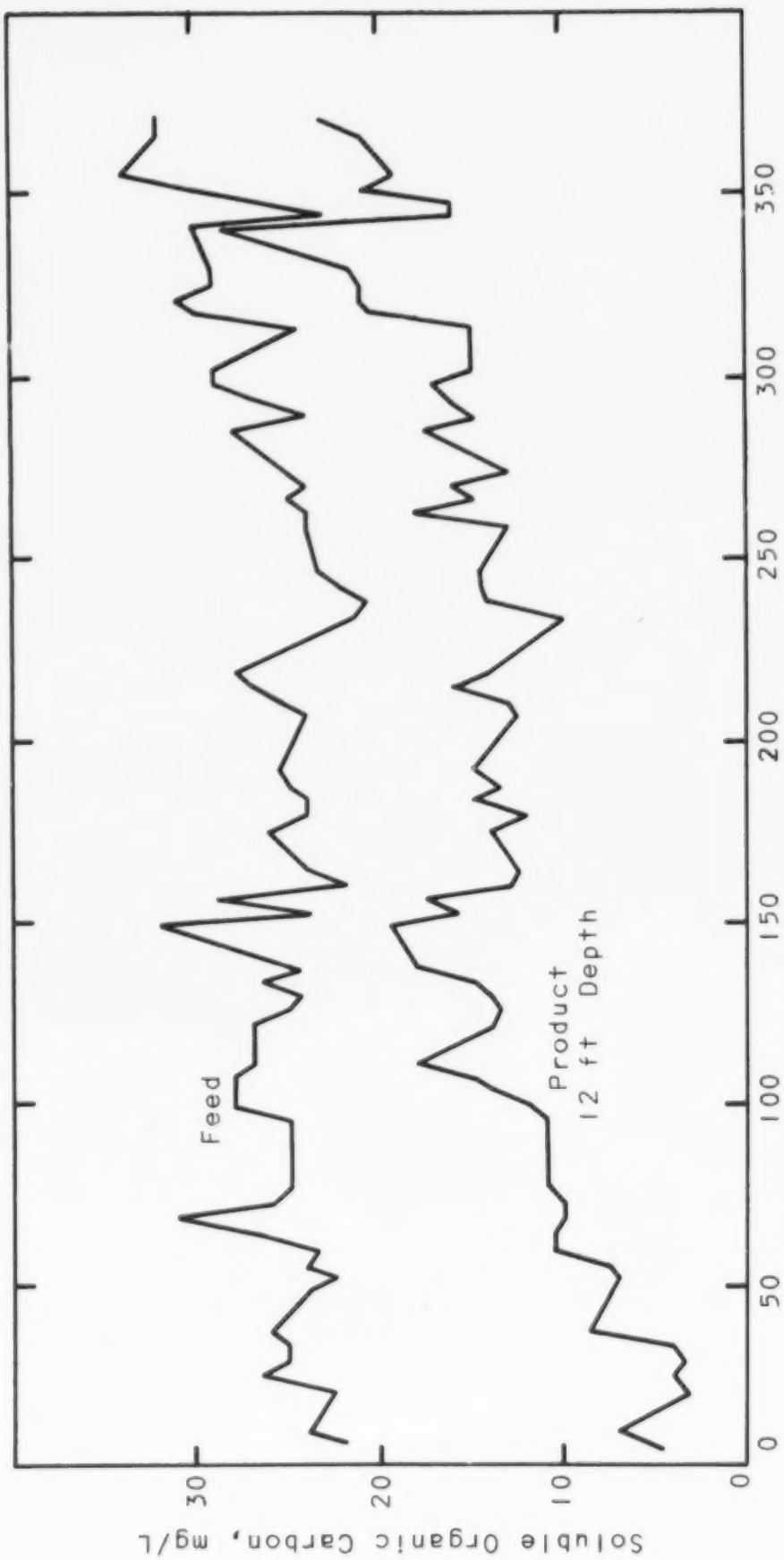


FIGURE 19. SOLUBLE ORGANIC REMOVAL FROM SECONDARY EFFLUENT IN EXPANDED BEDS OF ACTIVATED CARBON

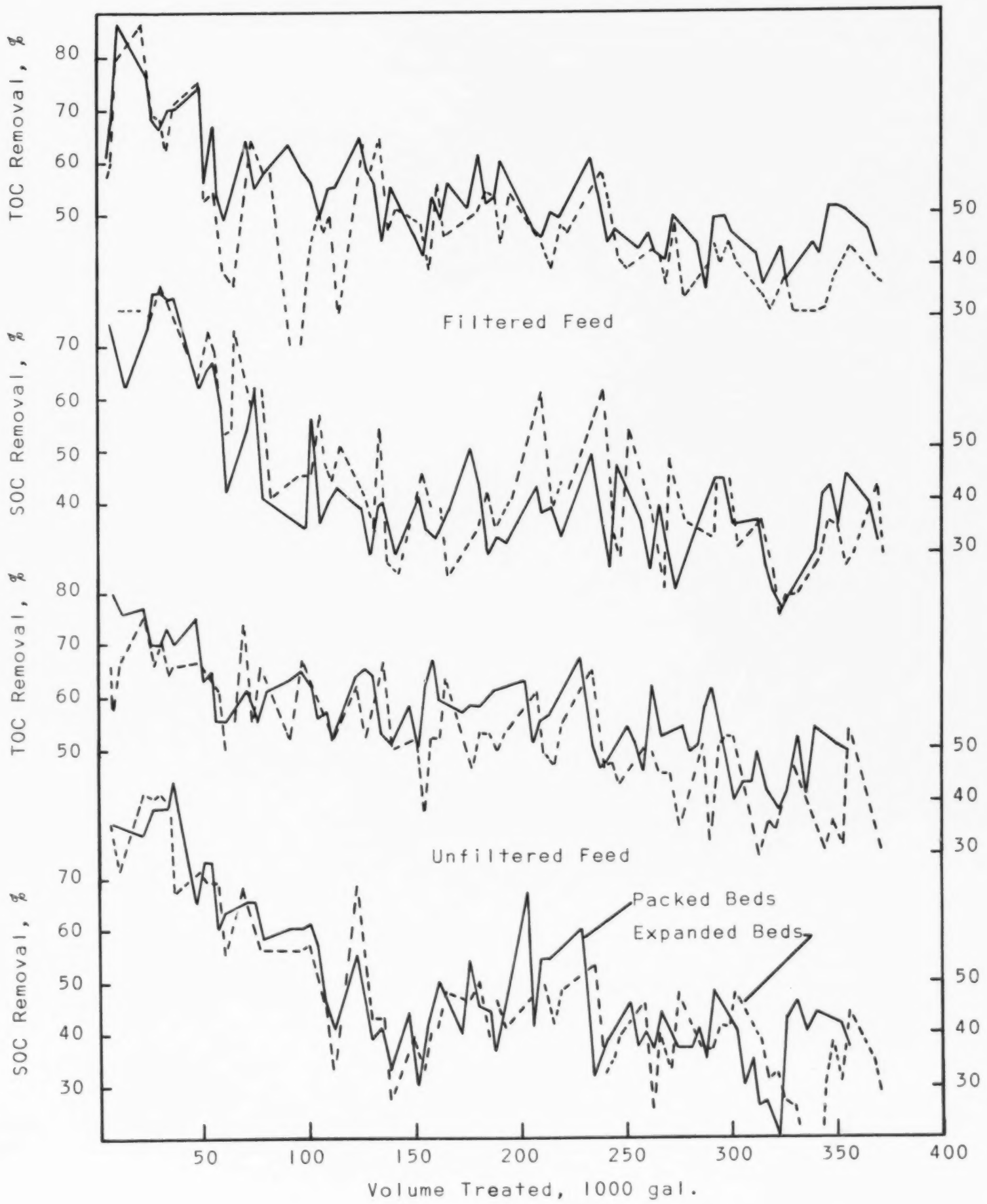


Figure 20. Fractional Organic Carbon Removal by Activated Carbon

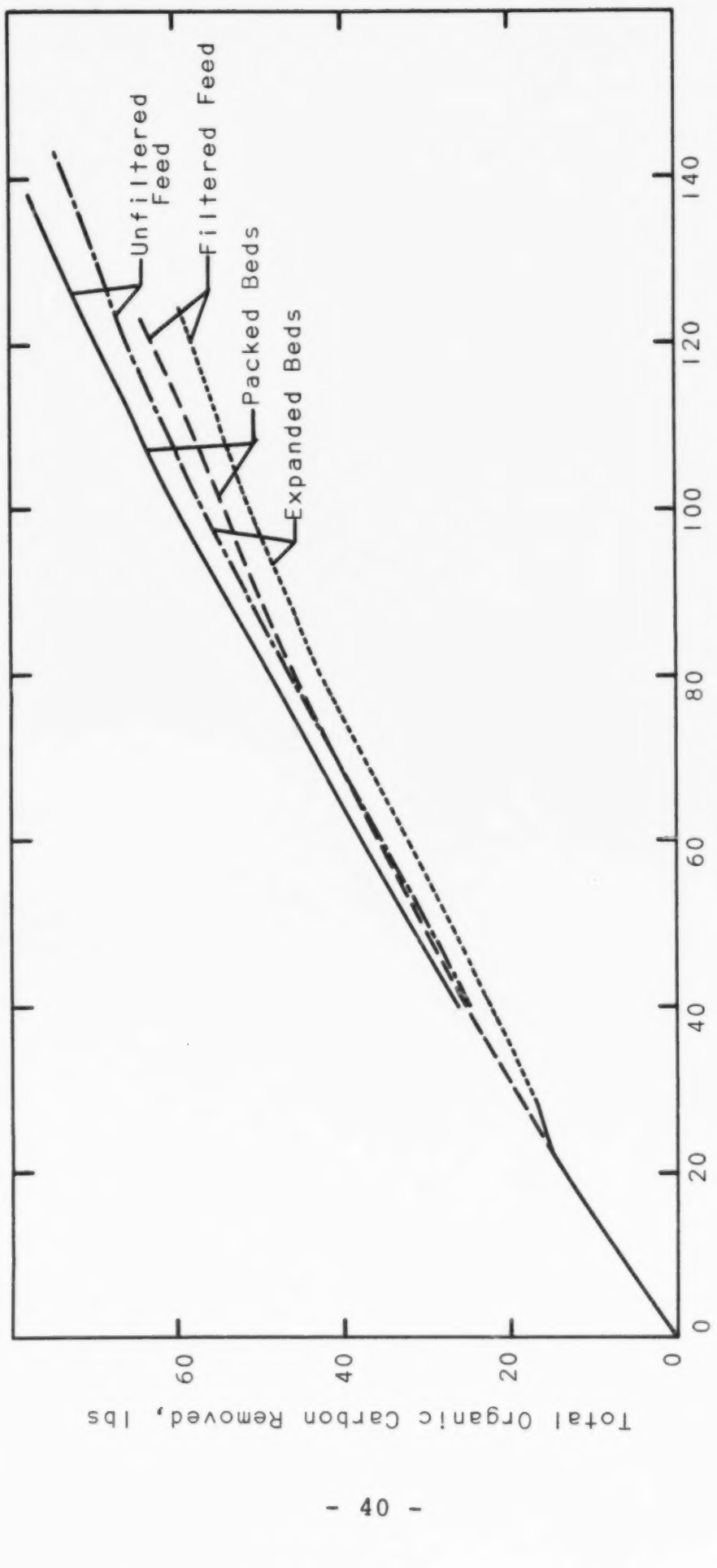


FIGURE 21. EFFECTIVENESS OF ACTIVATED CARBON FOR TOTAL ORGANIC REMOVAL IN A 12 FT BED

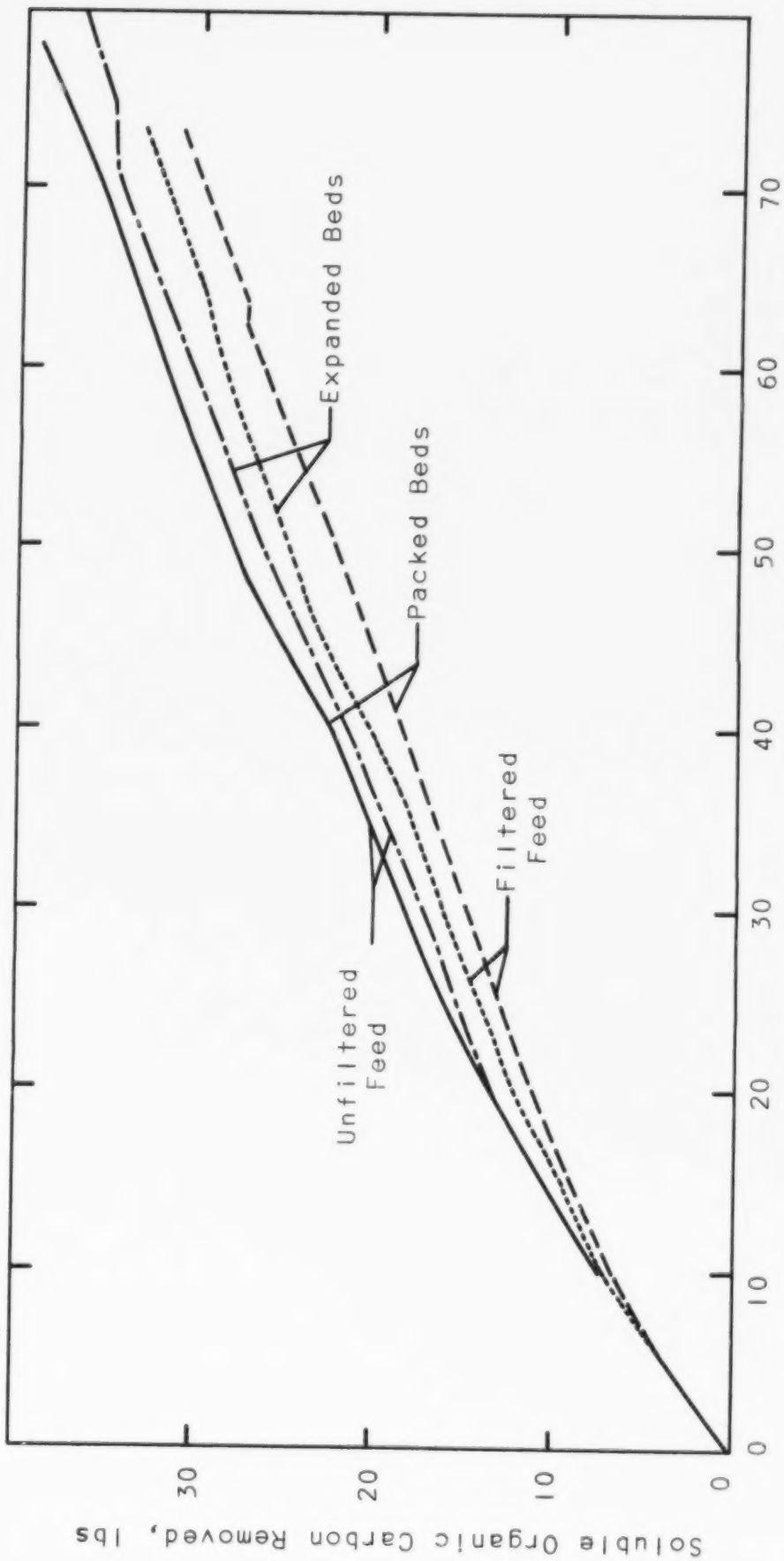


FIGURE 22. EFFECTIVENESS OF ACTIVATED CARBON FOR SOLUBLE ORGANIC REMOVAL IN A 12 FT BED

TABLE 3

Organic Carbon Removed From
Secondary Effluent by Activated Carbon in 12-ft Beds

| Pretreatment Bed Type | Filtered | | Unfiltered | |
|---|---|---|---|---|
| | Packed | Expanded | Packed | Expanded |
| Volume Treated, gal. | 369,669 | 372,465 | 355,547 | 370,662 |
| **Total Organic Carbon** | | | | |
| TOC Applied, lb | 122.93 | 123.36 | 137.71 | 143.55 |
| TOC Removed, lb | 64.60 | 59.45 | 78.10 | 74.68 |
| TOC Remaining, lb | 58.33 | 63.91 | 59.61 | 68.87 |
| Avg TOC in Product, mg/l | 18.9 | 20.6 | 20.1 | 22.3 |
| Avg TOC in Feed, mg/l | 39.8 | 39.7 | 46.5 | 46.5 |
| Percent TOC Removed | 52.6 | 48.1 | 57.0 | 52.0 |
| **Soluble Organic Carbon** | | | | |
| SOC Applied, lb | 74.06 | 74.45 | 78.88 | 81.89 |
| SOC Removed, lb | 31.28 | 33.33 | 39.14 | 37.39 |
| SOC Remaining, lb | 42.78 | 41.12 | 39.74 | 44.50 |
| Avg SOC in Product, mg/l | 13.9 | 13.3 | 13.4 | 14.4 |
| Avg SOC in Feed, mg/l | 24.0 | 24.1 | 26.6 | 26.5 |
| Percent SOC Removed | 42.2 | 44.7 | 49.6 | 45.7 |
| SOC Removed per lb Act. Carbon | 0.184 | 0.196 | 0.230 | 0.220 |

curve for the expanded bed treating filtered feed appears deceptively low as a result of some low removals early in the run. Figure 20 shows that removals for much of the run were nearly as good as for the packed bed. There may have been analytical errors in some of the early data points. Better removal by the packed beds were expected, because of their filtering action. That the difference in removal is so small is somewhat surprising. The expanded beds also accumulate solids, automatically adjusting for these added solids by an increase in bed height, with no significant increase in pressure or head loss.

For the removal of SOC, no clear difference in the effectiveness of the two bed configurations was observed. For the filtered feed, the expanded bed appears to be superior, possibly because of the use of the smaller carbon size and the resulting higher rate of adsorption. Had it been possible to prevent mixing of the carbon in the packed beds during operation, the overall adsorption driving force and, therefore, the removal effectiveness would have been larger in these beds. The beds were frequently disturbed, however, by cleaning and backwashing. The superiority of the expanded-bed configuration was not borne out by the data for unfiltered feed. In view of incomplete knowledge of the effects of suspended solids and biological activity on the carbon, it is concluded that the soluble-organic removal capability of the two types of contactors is essentially the same.

Both types of systems showed a greater removal of soluble organic carbon on a weight basis from the unfiltered secondary effluent than from the effluent which was passed through the dual media filter. Figure 15 shows, however, that the SOC was measurably higher in the wastewater before filtration. Greater removal from the unfiltered feed would, therefore, be expected. Biological degradation, which undoubtedly occurred during filtration, may also have altered the composition of some of the organic materials and, as a result, decreased their adsorbability.

As previously noted, the packed-beds were slightly more effective than the expanded-beds for removal of suspended solids. Figures 23, 24, 25, and 26 are plots of suspended solids in the feed and product waters as a function of volume treated for each of the four adsorber systems. The solids-removal effectiveness of the expanded beds was at times comparable to that of the packed beds, but on other occasions the expanded-beds appeared to retain little of the suspended solids. Although the dual media filter coupled with the activated carbon columns generally accomplished removal of a major part of the suspended solids, each of the systems invariably allowed a significant portion of these solids to escape in the product water. This trickling-filter effluent contains suspended solids consisting almost entirely of finely divided matter of which little or no fraction was settleable.

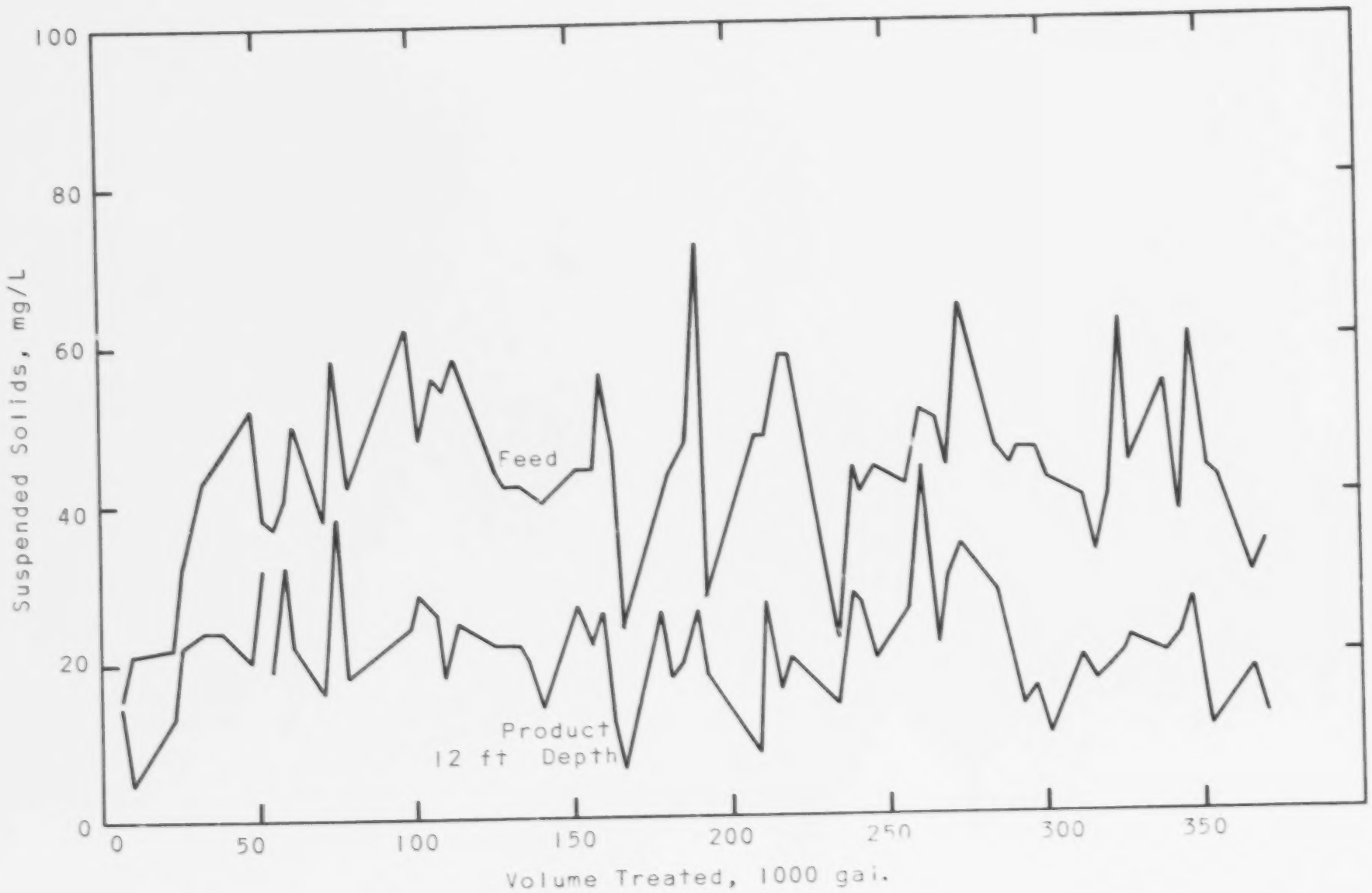


FIGURE 23. REMOVAL OF SUSPENDED SOLIDS FROM FILTERED SECONDARY EFFLUENT IN PACKED BEDS OF ACTIVATED CARBON

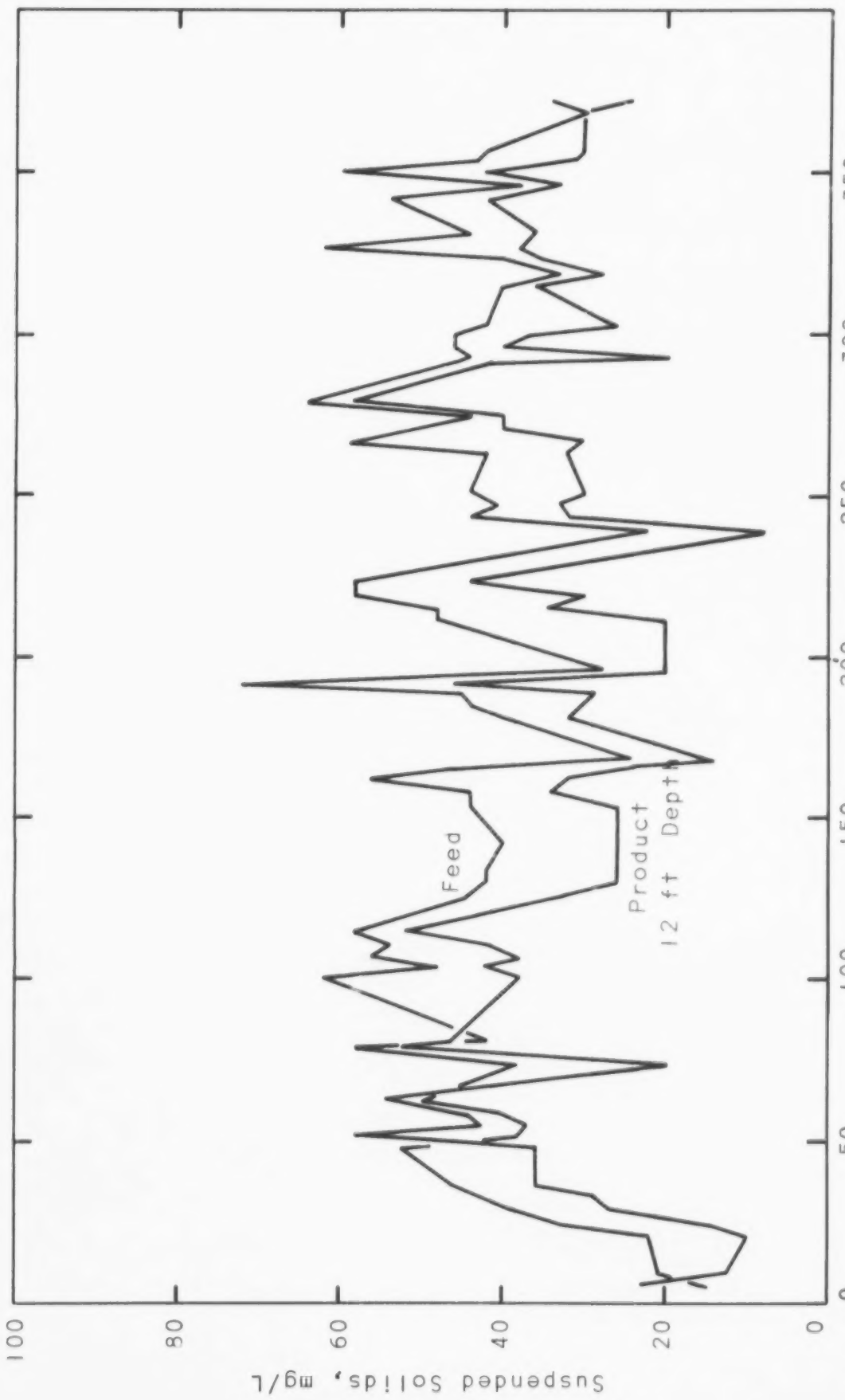


FIGURE 24. REMOVAL OF SUSPENDED SOLIDS FROM FILTERED SECONDARY EFFLUENT IN EXPANDED BEDS OF ACTIVATED CARBON

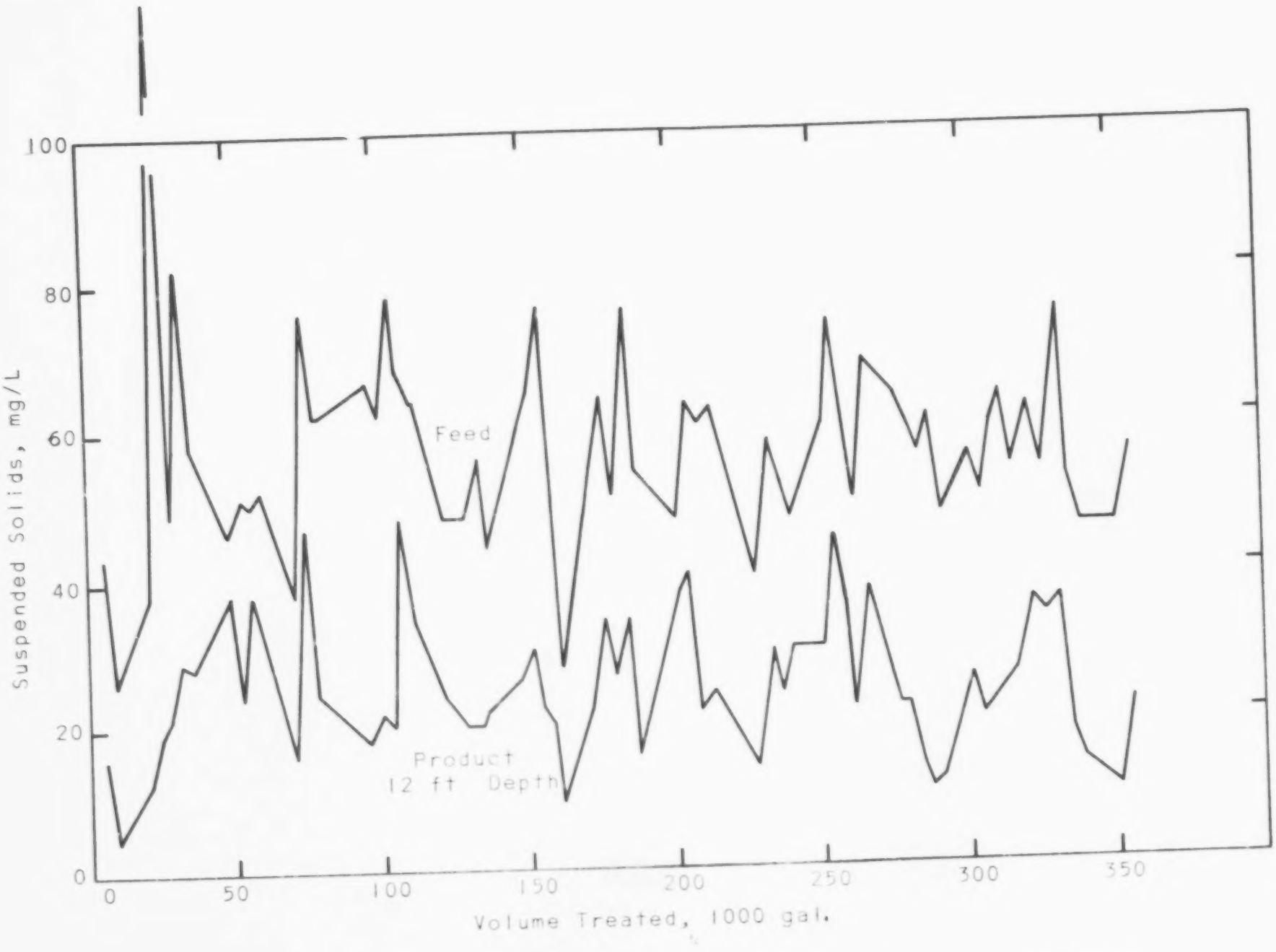


FIGURE 25. REMOVAL OF SUSPENDED SOLIDS FROM SECONDARY EFFLUENT IN PACKED BEDS OF ACTIVATED CARBON

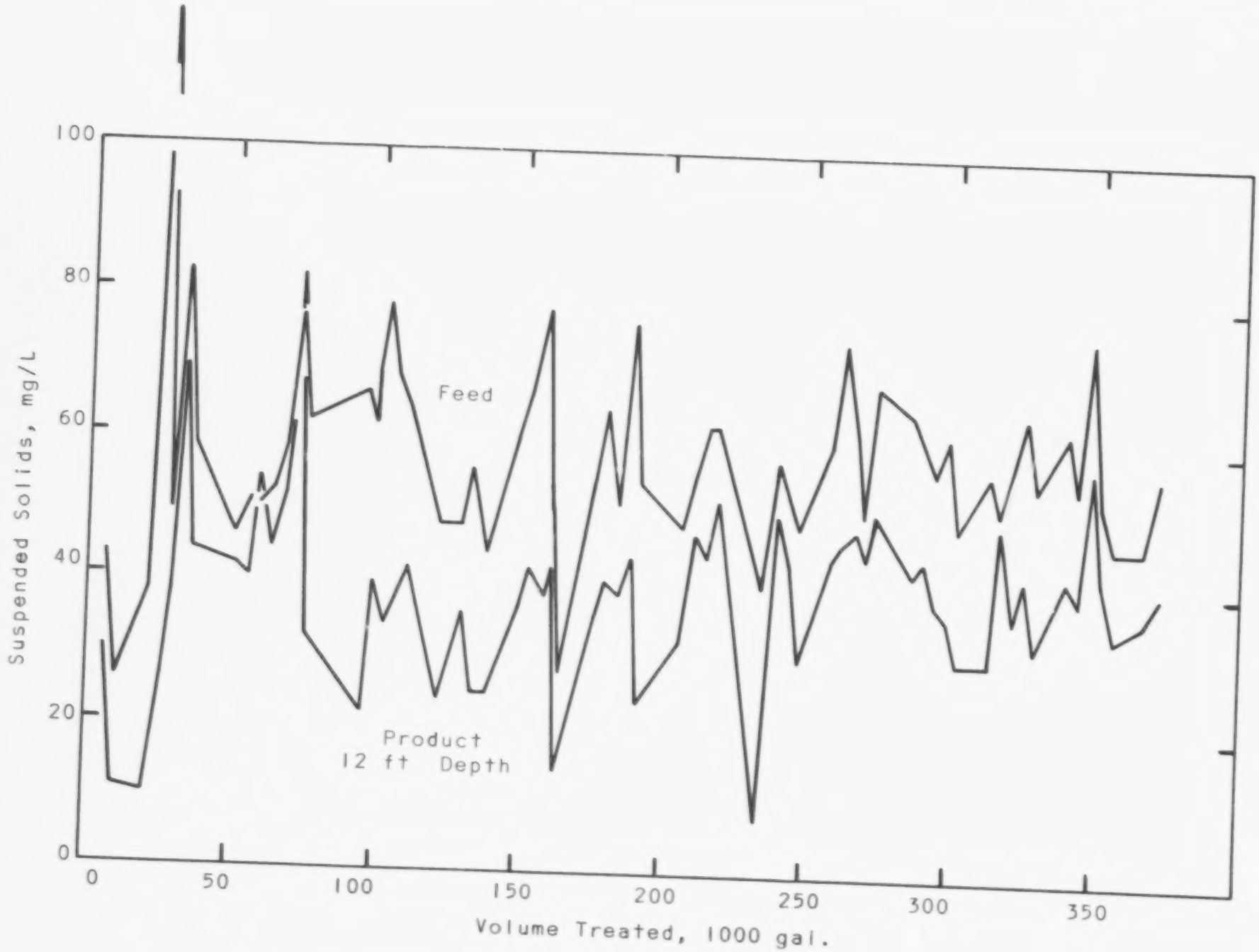


FIGURE 26. REMOVAL OF SUSPENDED SOLIDS FROM SECONDARY EFFLUENT IN EXPANDED BEDS OF ACTIVATED CARBON

## PILOT PROGRAM PHASE III

The third phase of the field comparisons of packed-bed and expanded-bed adsorbers was designed to evaluate the effects of more complete suspended solids removal on the sorption process. This phase also sought to determine whether the same type of biological films that had been noted with the expanded beds in Phase II would develop in expanded beds operating on a more completely clarified feed. An additional factor to be examined in Phase III was the effect of a greater total depth of carbon and the resulting longer contact time.

### Apparatus and Procedure

After a series of preliminary laboratory jar tests with secondary effluent, the pretreatment system chosen for solids removal in Phase III studies was chemical clarification with 50 mg/l of lime and 50 mg/l of ferric chloride ($FeCl_3 \cdot 6H_2O$) at a pH between 9.0 and 9.5, followed by settling and dual media filtration.

The pretreatment system is illustrated in Figure 27. The lime was fed from a calibrated dry feeder into a 55-gal. drum which served as a rapid-mix tank. A solution of ferric chloride was also fed to this tank. The chemically treated secondary effluent was then transferred from the rapid-mix tank through a line discharging at the center of a 250-gal. tank which served as the clarifier. Following sedimentation, the water from the clarifier was fed to the sand filter.

At the beginning of each day of operation, sludge was siphoned from the bottom of the clarifier, and the filter was air-scoured and back flushed with water to remove accumulated solids. Since the pH of the wastewater was maintained at 9.0 to 9.5 during the pretreatment, it was readjusted to the original level of 7.0 to 7.5 by the addition of sulfuric acid in a 250-gal. holding tank prior to being fed to the adsorbers.

Each of the eight experimental adsorbers constructed in Phase II was charged with 85 lb of 12x40 mesh activated carbon at the beginning of the Phase III study, yielding a settled depth of 6 ft of carbon in each adsorber. The four packed-bed adsorbers were then connected in series to give a total packed-bed depth of 24 ft. The expanded-bed adsorbers were also connected in series.

Clarified feed from the holding tank was pumped to each of the column systems by separate pumps, and daily composite samples were taken of the feed and of the product water from each of the eight individual adsorbers. All analytical determinations were performed in the same manner as described in the foregoing discussion of the Phase II studies. The measurement and control systems were also the same as described in Phase II. Daily observations were made of flow rate, volumes, and pressures. Appropriate adjustments and cleanings were made.

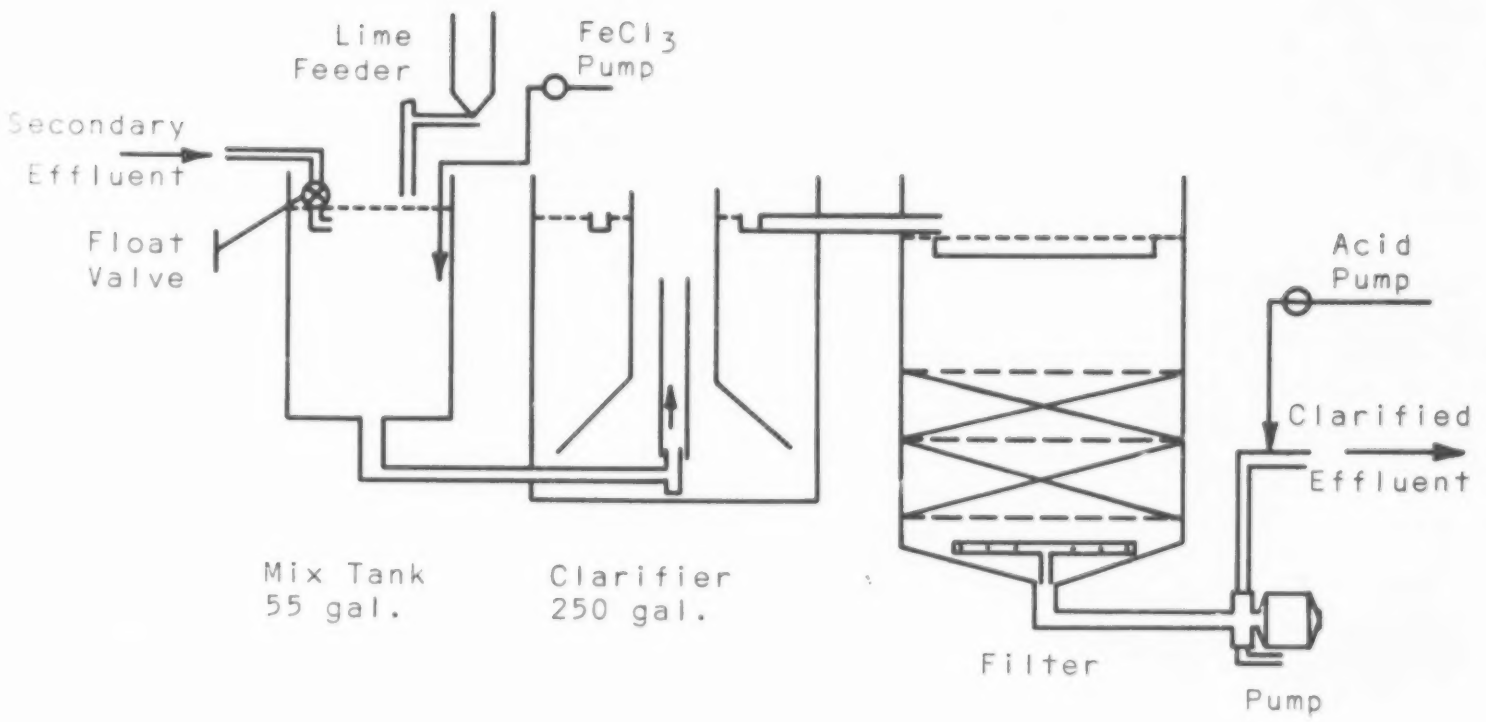


FIGURE 27. DIAGRAM OF APPARATUS FOR CLARIFICATION OF SECONDARY EFFLUENT

## Experimental Results and Discussion

Clarification, while not as effective as desired, did reduce the suspended solids below levels obtainable with filtration alone. Suspended solids concentrations for the secondary effluent, clarified feed and products are shown in Figure 28. An interesting observation from the data in Figure 28 is that the 24-ft-deep packed-bed adsorber provided very little more removal of suspended solids than the equivalent expanded-bed system. It is also quite apparent that further clarification would be required for any reuse application calling for a clear water. Operating pressure in the 24-ft packed-bed system with a clarified feed are shown, in Figure 29 to follow a similar pattern to that observed in Phase II. The fact that the solids removal accomplished by chemical clarification was incomplete prohibited operation of the four-column packed-bed system without frequent cleanings. None of the expanded beds studied in Phase II was intentionally cleaned although the accidental introduction of air with the feed accomplished some degree of cleaning. These incidents are noted in Figure 29.

Organic removal data for the two systems are presented in Figure 30 through 33. Cumulative removal of organic materials by the packed-bed and expanded-bed systems for both 12 and 24-ft settled depths of carbon are presented in Figure 34 and 35, and are summarized in Table 4. The plots of cumulative removal indicate that the packed beds removed somewhat more TOC and slightly more SOC than the expanded beds. The enhanced removal of TOC by the packed beds is in part attributable to the filtering action of these beds. However, some of the difference in both TOC and SOC removal can be attributed to the accidental loss of carbon from the expanded beds during the run, which would lead to a corresponding reduction in performance of this system. Some carbon was carried from the expanded-bed system by inadvertent introduction of air with the column feed. The carbon loss from the beds amounted to about 9% of that in the four-column system, as estimated at the end of the run. Points noted in Figure 29 indicate when the carbon losses occurred. Table 4 shows that, despite the loss of activated carbon from the expanded-bed system, the removal of SOC during the course of the run was 96% of that obtained in the packed-bed system. As in Phase II, the mode of contacting appears to have little effect on the effectiveness of the adsorption process.

The data presented in Table 4 indicate that about 3/4 of the TOC and SOC removed in the four-column adsorption systems (24 ft of carbon) was removed in the first two columns. The average product SOC values of 5.9 mg/l and 6.7 mg/l were within about 2 mg/l of the values observed throughout most of the course of the experiment. Few analyses, even at the beginning of the run, resulted in product SOC values of less than 4 mg/l, indicating that there was a small initial breakthrough even for the total settled depth of carbon of 24 ft. This initial leakage is probably comprised of non-adsorbing or slightly adsorbing organic substances.

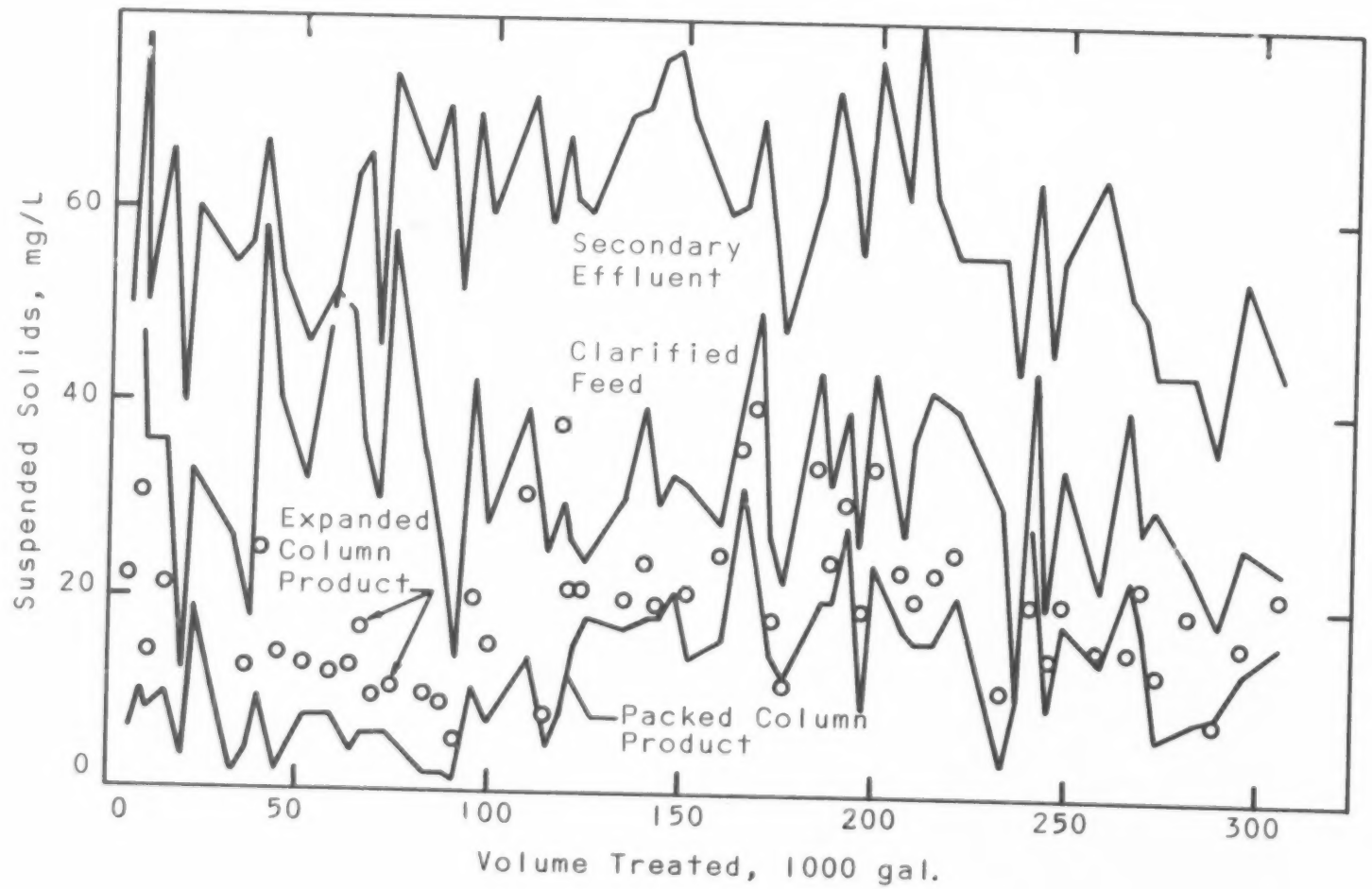


FIGURE 28. REMOVAL OF SUSPENDED SOLIDS DURING CLARIFICATION AND CARBON TREATMENT OF SECONDARY EFFLUENT

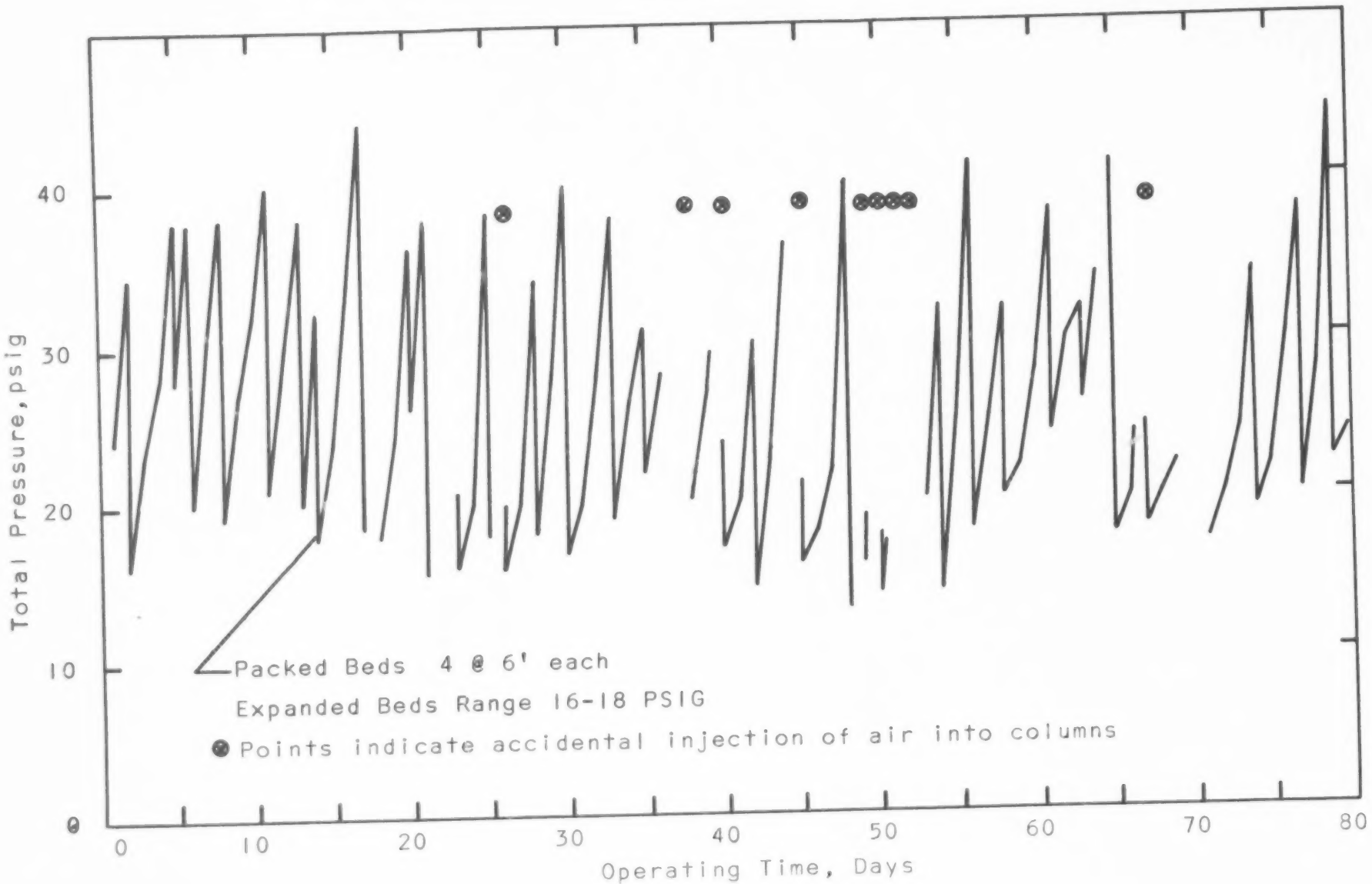


FIGURE 29. PRESSURE ON 24 FT OF ACTIVATED CARBON TREATING CLARIFIED FEED

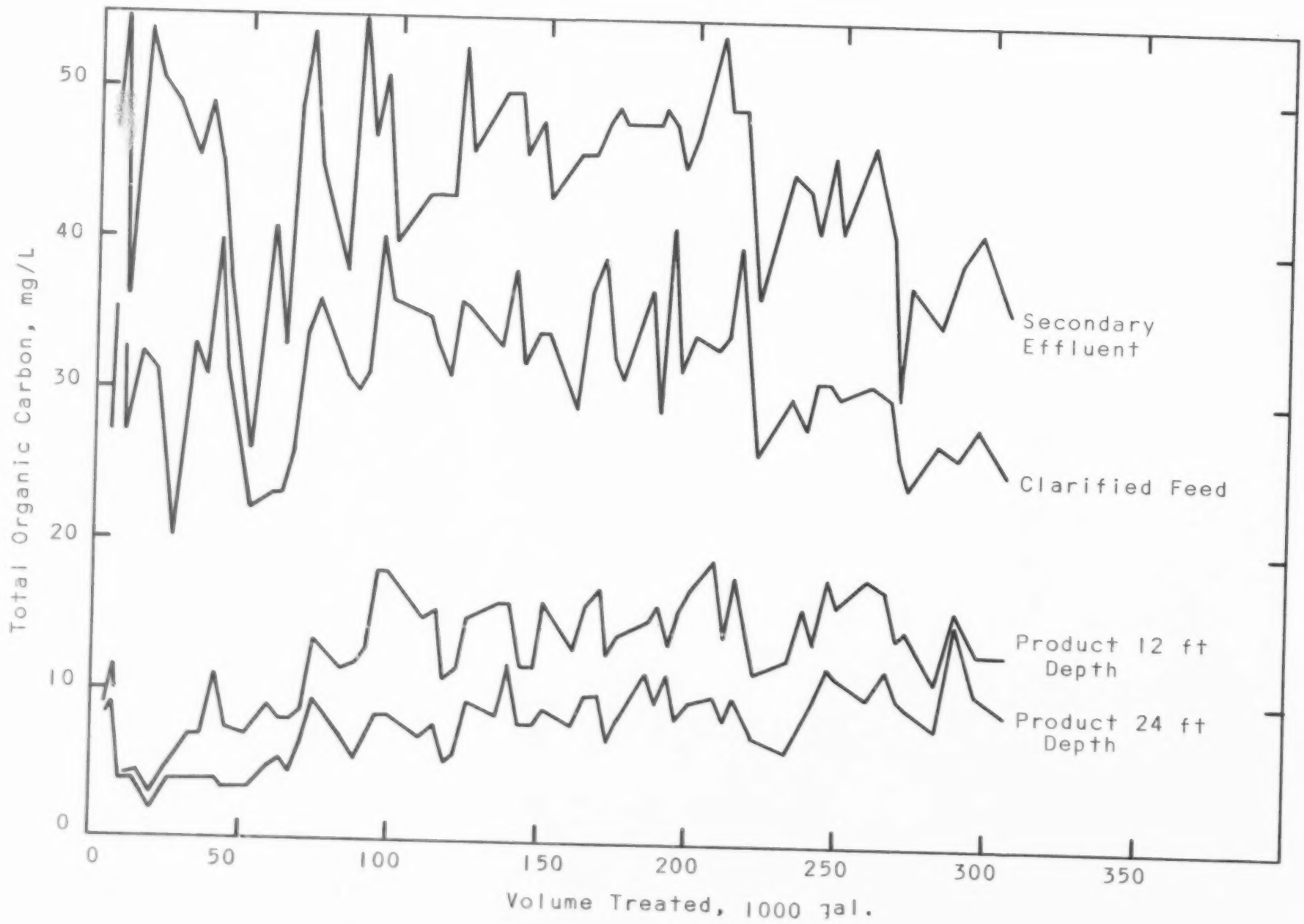


FIGURE 30. TOTAL ORGANIC REMOVAL FROM CLARIFIED SECONDARY EFFLUENT IN PACKED BEDS OF ACTIVATED CARBON

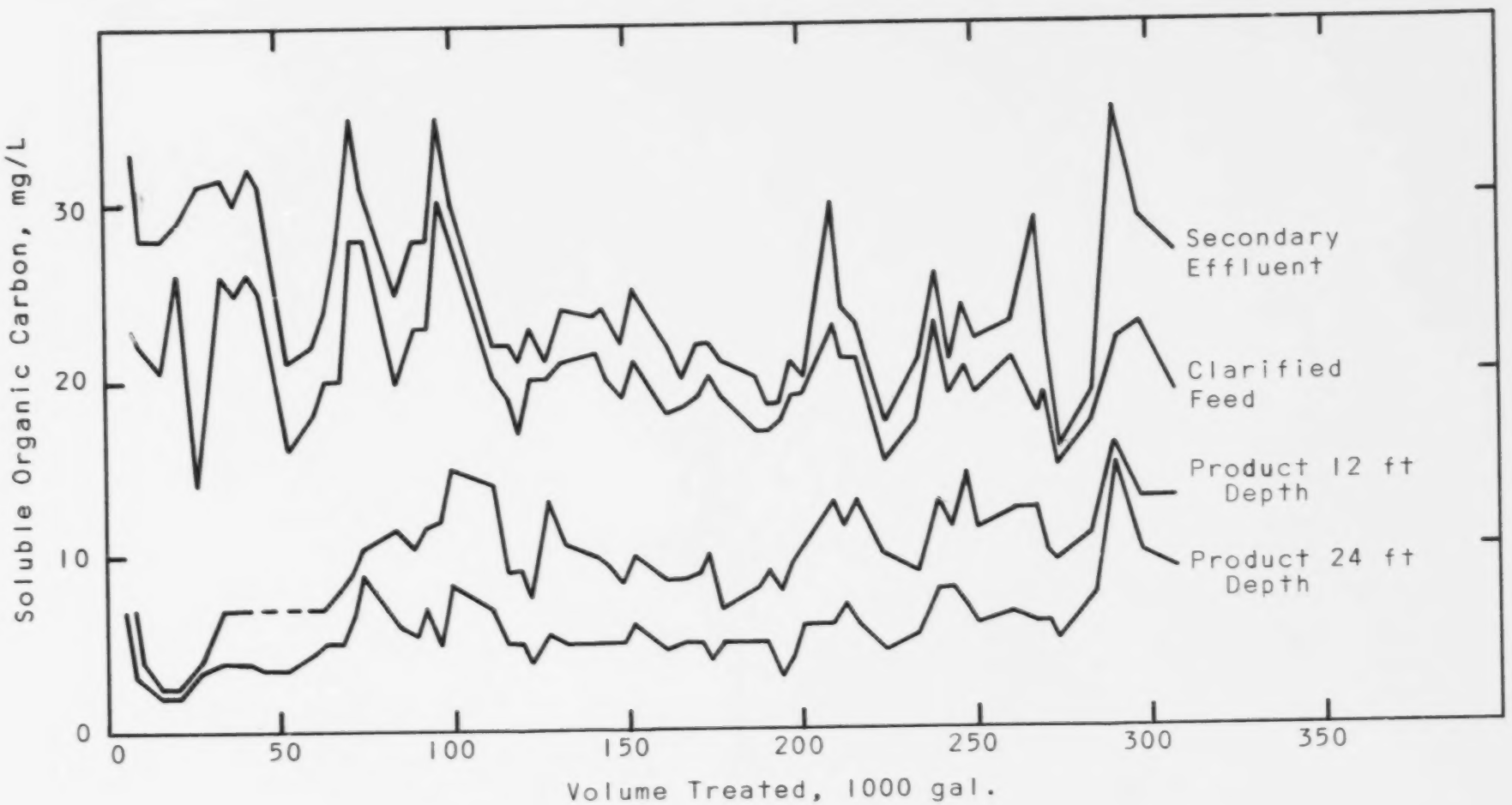


FIGURE 31. SOLUBLE ORGANIC REMOVAL FROM CLARIFIED SECONDARY EFFLUENT IN PACKED BEDS OF ACTIVATED CARBON

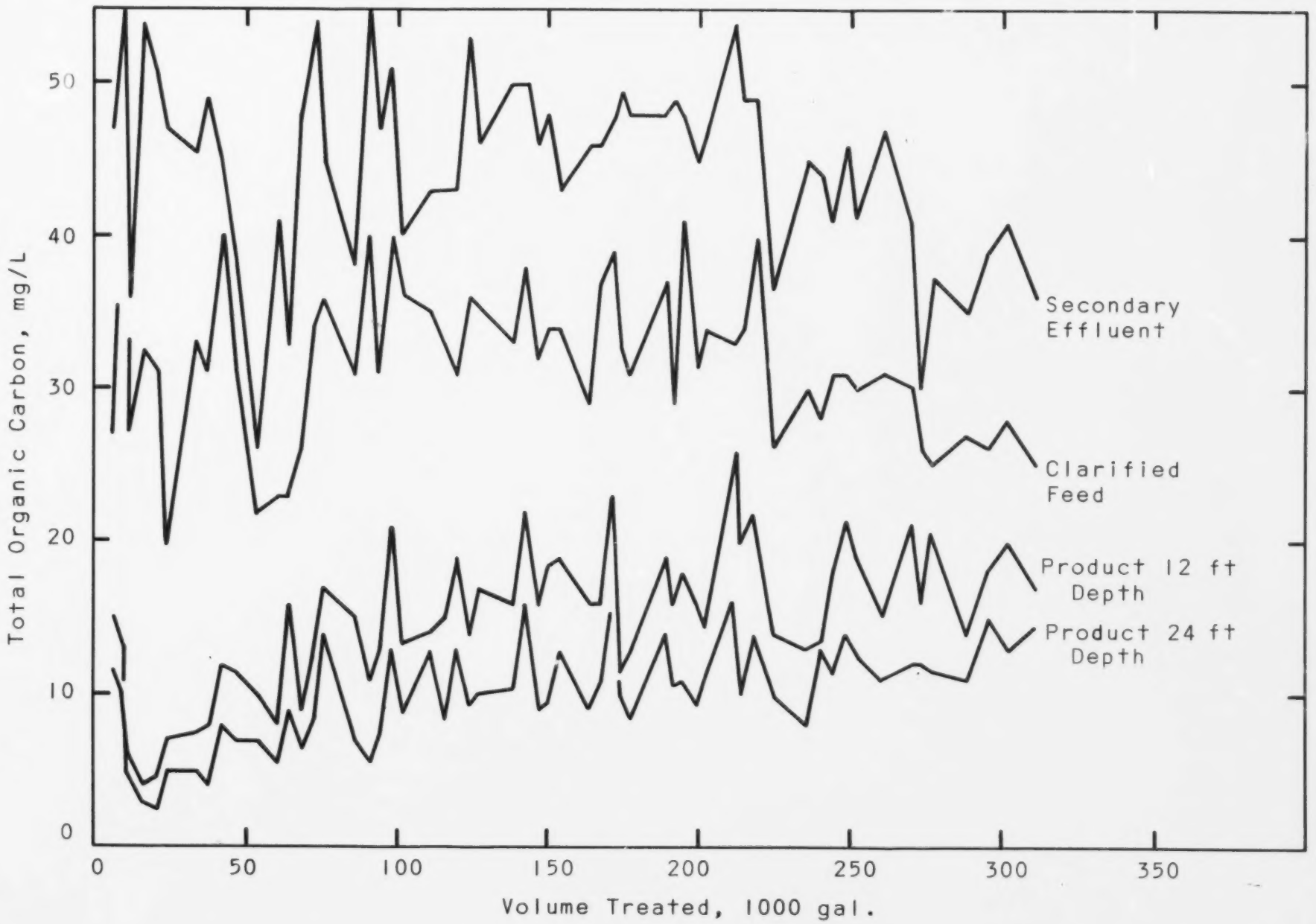


FIGURE 32. TOTAL ORGANIC REMOVAL FROM CLARIFIED SECONDARY EFFLUENT IN EXPANDED BEDS OF ACTIVATED CARBON

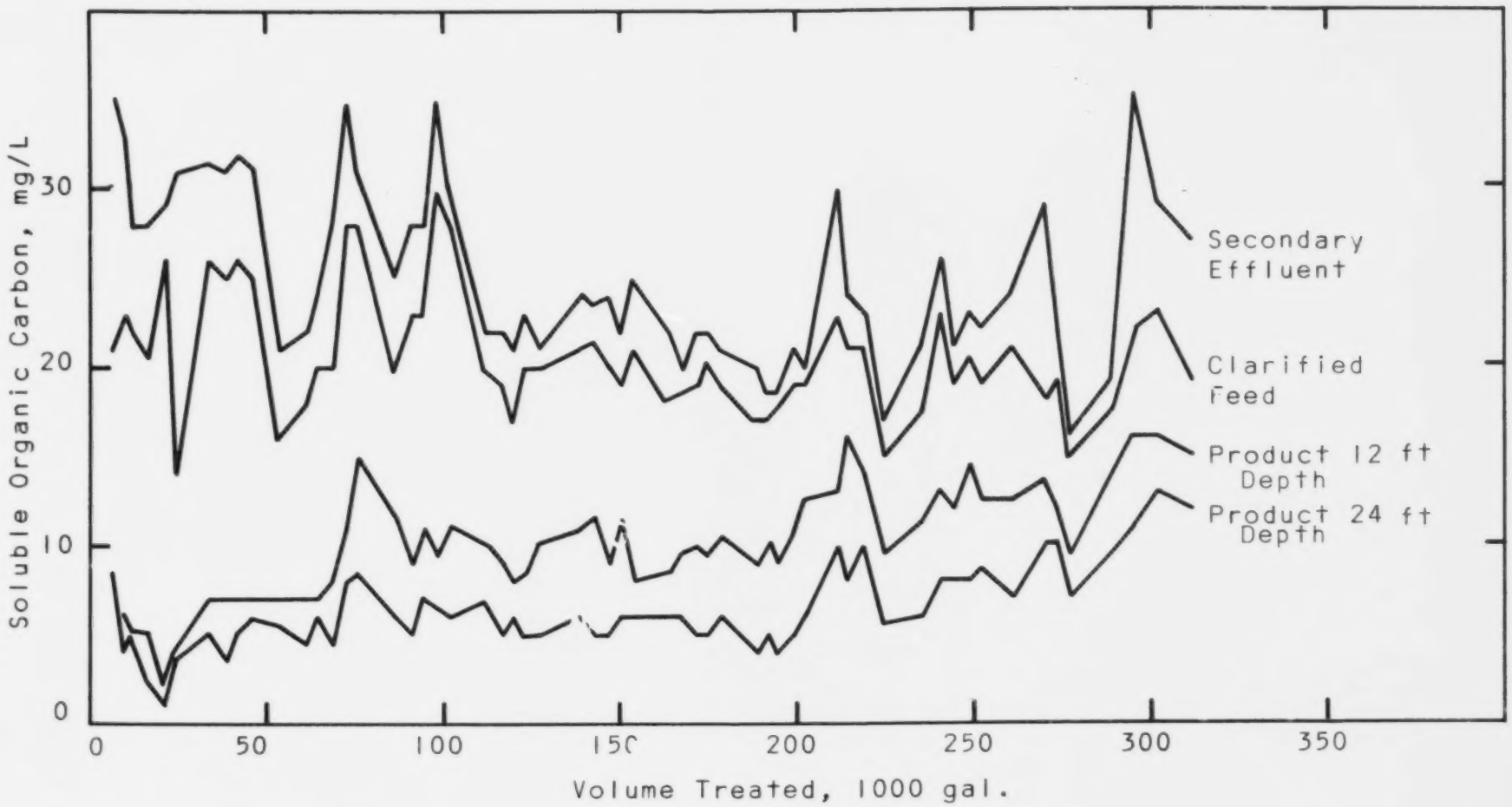


FIGURE 33. SOLUBLE ORGANIC REMOVAL FROM CLARIFIED EFFLUENT IN EXPANDED BEDS OF ACTIVATED CARBON

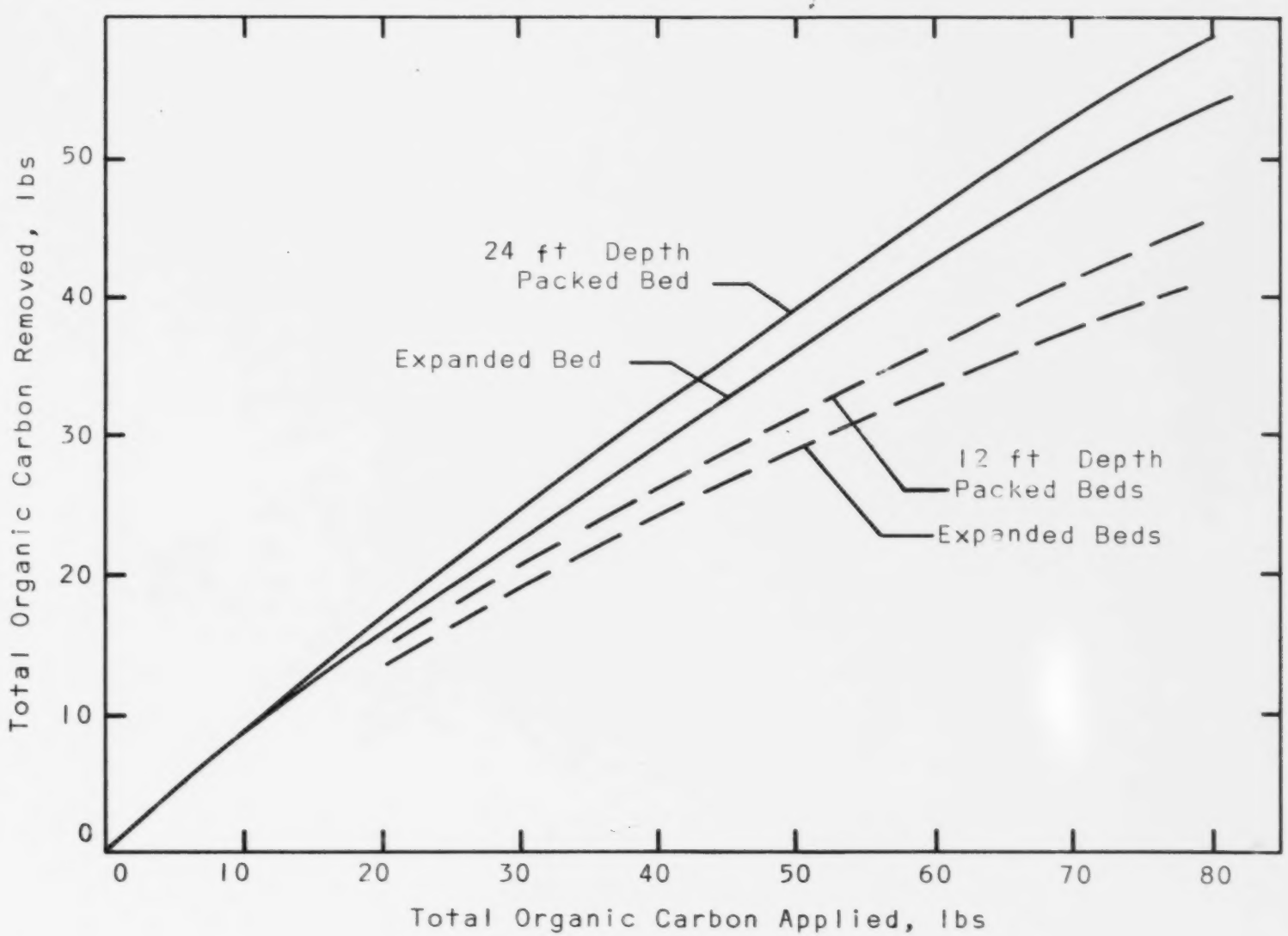


FIGURE 34. EFFECTIVENESS OF ACTIVATED CARBON FOR TOTAL ORGANIC REMOVAL FROM CLARIFIED SECONDARY EFFLUENT

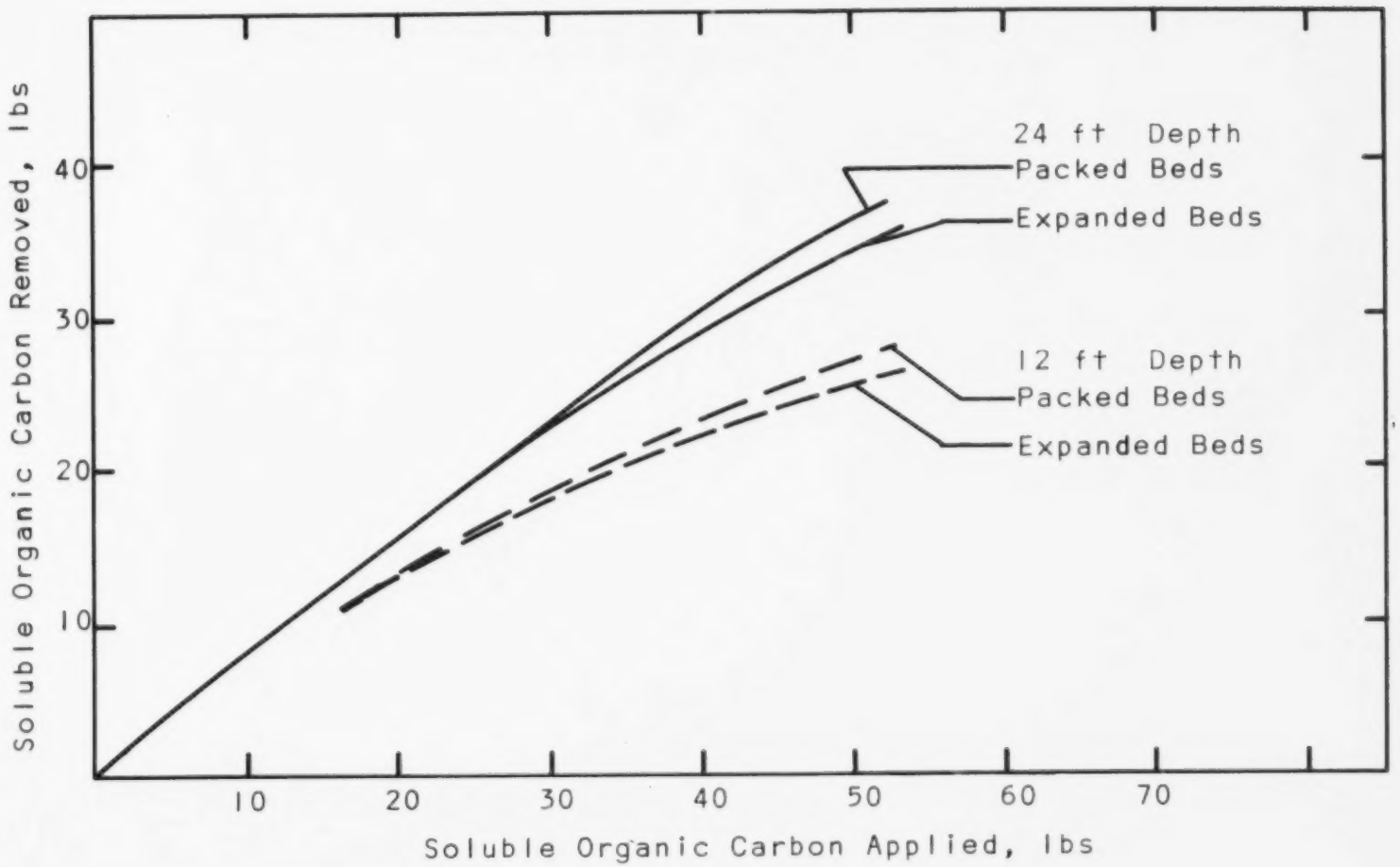


FIGURE 35. EFFECTIVENESS OF ACTIVATED CARBON COLUMNS FOR SOLUBLE ORGANIC REMOVAL FROM CLARIFIED SECONDARY EFFLUENT

TABLE 4

Organic Carbon Removal from Clarified Secondary Effluent by Activated Carbon in 24-ft Beds

| | Packed Columns | | | Expanded Columns | | |
|---|---|---|---|---|---|---|
| Volume Treated, gal. | 307,365 | | | 313,756 | | |
| **Total Organic Carbon** | | | | | | |
| TOC Applied, lb | 79.550 | | | 81.296 | 81.296 | |
| Column No. | (1,2) | (3,4) | (Total) | (1,2) | (3,4) | (Total) |
| TOC Removed, lb | 45.842 | 13.034 | 58.876 | 41.569 | 13.052 | 54.621 |
| TOC Remaining, lb | 33.708 | | 20.674 | 39.727 | | 26.675 |
| Avg TOC in Product, mg/l | 13.4 | | 8.06 | 15.18 | | 10.19 |
| Avg TOC in Feed, mg/l | 31.03 | | | 31.05 | | |
| Percent TOC Removal | 57.6 | 16.4 | 74.0 | 51.1 | 16.1 | 67.2 |
| **Soluble Organic Carbon** | | | | | | |
| SOC Applied, lb | 52.325 | | | 53.334 | 53.334 | |
| Column No. | (1,2) | (3,4) | (Total) | (1,2) | (3,4) | (Total) |
| SOC Removed, lb | 27.646 | 9.732 | 37.378 | 26.122 | 9.671 | 35.793 |
| SOC Remaining, lb | 24.679 | | 14.947 | 27.212 | | 17.541 |
| Avg SOC in Product, mg/l | 9.62 | | 5.95 | 10.39 | | 6.70 |
| Avg SOC in Feed, mg/l | 20.41 | | | 20.38 | | |
| Percent SOC Removal | 52.8 | 18.6 | 71.4 | 49.0 | 18.1 | 67.1 |
| lb SOC Removed/lb Carbon | 0.163 | 0.056 | | 0.154 | 0.056 | |

The 170 lb of activated carbon contained in the third and fourth columns of each system removed less than 10 lb of SOC and about 13 lb of TOC in treating over 300,000 gal. of effluent from the first and second columns in each system. The effluent from the first two columns contained an average SOC of about 10 mg/l. Therefore, the first 170 lb of carbon in each system removed about half of the SOC applied, while the second 170 lb removed somewhat less than half of the SOC remaining. Worthy of note is the fact that the first 12-ft settled depth of carbon in each of the two systems operating on the clarified feed had average removal rates of about 0.10 lb of SOC per 1,000 lb carbon per hour, approximately the same as obtained for each of the four 12-ft adsorption systems studied in Phase II.

A point to be noted is that SOC, as well as TOC, was removed both by the filtration pretreatment carried out in the Phase II studies, and by the more extensive pretreatment of the Phase III studies. As shown in Table 3, the difference between the SOC values of 26.5 mg/l for the raw secondary effluent and 24.1 mg/l for the filtered secondary effluent resulted from the pretreatment step. Figure 33 illustrates the consistent removal of about the same amount of SOC during coagulation-filtration pretreatment. Some biological activity was apparent in the pretreatment units, as it was in the activated carbon columns. This activity might have contributed to the SOC removal observed during pretreatment.

As in Phase II, the greatest difference between the packed-bed and expanded-bed adsorption systems was the necessity for much more frequent cleaning of the former system due to clogging and build up of excessive head losses. Figure 29 shows the seriousness of this problem. The first column in the packed-bed system required cleaning 22 times over the course of the Phase III pilot field study, while the expanded-bed system was not cleaned intentionally during the entire study. Some accidental cleaning of the expanded beds was provided on several occasions when the clarification system failed to produce sufficient volumes of water to maintain the flow in the adsorbers. When this happened, air was pumped into the adsorbers through the influent lines, thus serving to clean the carbon. This accidental cleaning was, of course, not nearly equivalent to that provided by air scouring and backwashing. Also, because it occurred during times when the adsorbers were unattended, some transfer of carbon from one column to another in the four-column series took place and some carbon was lost from the system.

## ANALYSIS OF SPENT CARBON

At the conclusion of operation of the four adsorber systems studied in Phase II and the two systems studied in Phase III, the spent carbon in each of the eight columns was thoroughly cleaned *in situ* by air scouring, then removed and allowed to drain. Representative 1-gal. samples taken from each of the drained carbons, were analyzed for moisture, volatile matter, and ash. Dried samples from Phase II were checked for sieve analysis. Iodine numbers were determined on

the dried and devolatilized samples from both phases of study. In addition, samples of the spent carbons from each column in Phase II were extracted with chloroform and methanol in a preliminary attempt to characterize the adsorbed substances.

Moisture and Volatile Matter

Each of the columns originally had been charged with 85 lb of fresh activated carbon. Any carbon lost from a column during cleaning operations over the course of the Phase II studies was recovered and returned to that column. This recovery was accomplished by collecting and settling the backwash waters. For all practical purposes, the activated carbon sampled at the end of the run was the same carbon present initially. In Phase III, there was some loss of carbon from the expanded-bed system. The weights of the carbon removed from each of the eight columns after operation are listed in Table 5, along with the calculated weights after drying and devolatilizing. Moisture, volatile matter and ash contents are presented in Table 6.

Table 6 shows that the spent carbon from all of the columns in Phase II was generally similar. The drained carbon contained about 35% moisture, determined as weight loss in about 2 hours at 140°C, and all of the dried carbon samples contained from 13% to 18% volatile matter, determined as weight loss on heating to 900°C in an inert atmosphere.

With one exception, the dried carbon from the first column of each of the four pairs contained more volatile matter than the second. This result was expected because the first column was in contact with a more concentrated feed solution. The amounts of volatile matter on the spent carbon are in the same range as the calculated amounts of SOC removed from the secondary effluent during the Phase II treatment operation, as discussed previously. The amount of SOC removed was calculated to be about 17% to 22% of the total original weight of activated carbon charged to the two columns in each adsorber system. At the 900°C temperature used for liberation of volatile matter, organic compounds undergo dehydration, decomposition and vaporization to leave various amounts of carbonaceous residue. Although the weight loss incurred during heating tends to approach the weight of organic material adsorbed, the unknown extent of carbon deposition prevents the drawing of any firm conclusion in this regard. The analyses indicate that in all cases the weight of the dry, de-volatilized spent carbons is greater by from 5% to 17% than the weight of the original activated carbon charged. These increases in weight are probably due in large part to the carbonization reaction, and in some part to the deposition of inorganic substances.

Table 6 shows that the moisture contents for the carbon samples from Phase III were about 45%, substantially higher than those from Phase II. Volatile content was significantly less

TABLE 5

Weight, Moisture and Volatile Content of Spent Carbon From Column Tests

| Column Designation* | Weight of Drained Carbon lb | Weight of Dried Carbon lb | Weight of Devolatilized Carbon, lb Column | System |
|---|---|---|---|---|
| (Phase II, 2-column systems) | | | | |
| PCU 1 | 173.5 | 113.4 | 93.8 | |
| PCU 2 | 168.0 | 110.2 | 92.1 | 185.9 |
| PCF 1 | 188.3 | 118.4 | 100.5 | |
| PCF 2 | 162.8 | 103.0 | 89.6 | 190.1 |
| ECU 1 | 176.9 | 110.6 | 91.5 | |
| ECU 2 | 178.8 | 114.0 | 96.5 | 188.0 |
| ECF 1 | 155.4 | 108.0 | 90.2 | |
| ECF 2 | 167.9 | 109.3 | 90.0 | 180.2 |
| (Phase III, 4-column systems) | | | | |
| PC 1 | 160.3 | 94.9 | 82.4 | |
| PC 2 | 156.2 | 90.3 | 79.0 | |
| PC 3 | 188.2 | 100.3 | 91.8 | |
| PC 4 | 172.8 | 90.6 | 85.5 | 338.7 |
| EC 1 | 130.7 | 78.6 | 68.3 | |
| EC 2 | 155.5 | 88.6 | 77.9 | |
| EC 3 | 151.6 | 85.9 | 77.6 | |
| EC 4 | 142.1 | 74.3 | 68.7 | |
| EC Carryover | 83.6 | 33.6 | 31.6 | 324.1 |

*PCU - Packed column, unfiltered feed
PCF - Packed column, filtered feed
ECU - Expanded column, unfiltered feed
ECF - Expanded column, filtered feed
PC - Packed column, chemically clarified feed
EC - Expanded column, chemically clarified feed

Each column initially charged with 85 lb activated carbon

TABLE 6

Analysis of Spent Carbon from Column Tests

| Sample Identification | Moisture on Drained Carbon Wt % | Volatile Matter on Dried Carbon Wt % | Ash On Devolatilized Carbon % | Ash On Dried Carbon Wt % | Ash Calc on Devol Basis Wt % |
|---|---|---|---|---|---|
| | Phase II, 2-Column Systems | | | | |
| PCU 1 | 34.6 | 17.4 | 7.1 | 5.9 | 7.1 |
| | | 15.8* | | | |
| PCU 2 | 34.4 | 16.5 | 7.5 | 6.0 | 7.2 |
| | | 11.1 | | 6.3* | 7.5* |
| PCF 1 | 37.1 | 15.1 | 7.1 | 6.0 | 7.1 |
| | | 14.9 | | | |
| PCF 2 | 36.7 | 13.4 | 7.2 | 6.2 | 6.9 |
| | | 13.0 | | | |
| ECU 1 | 37.5 | 17.3 | 6.8 | 6.0 | 7.2 |
| | | 16.2 | | 5.9 | 7.1 |
| ECU 2 | 36.2 | 15.4 | 7.3 | 6.5 | 7.7 |
| | | 15.8 | | | |
| ECF 1 | 30.5 | 16.5 | | 6.0 | 7.2 |
| | | 16.1 | | 6.0 | 7.2 |
| ECF 2 | 34.8 | 17.7 | 7.6 | 6.3 | 7.7 |
| | | 14.9 | | | |
| | Phase III, 4-Column Systems | | | | |
| PC 1 | 42.4 | 13.2 | | 7.1 | 8.2 |
| PC 2 | 43.5 | 12.5 | | 6.9 | 7.9 |
| PC 3 | 46.7 | 8.5 | | 6.7 | 7.3' |
| PC 4 | 47.5 | 5.5 | | 9.2 | 9.7 |
| EC 1 | 39.8 | 13.1 | | 5.8 | 6.7 |
| EC 2 | 43.0 | 12.1 | | 6.3 | 7.1 |
| EC 3 | 45.5 | 9.5 | | 6.2 | 6.8 |
| EC 4 | 47.8 | 7.3 | | 6.1 | 6.6 |
| EC Carryover | 59.8 | 6.0 | | | |

*Results of duplicate analyses

than observed in Phase II. The volatile content declined significantly from the first to the fourth contactor in both packed and expanded beds. This expected result is in agreement with SOC removals observed during Phase III operation.

Ash Content

The ash contents of the spent carbons in Phase II showed a 15% to 31% increase over the value of 5.9% by weight for the virgin carbon. Results from the packed bed in Phase III were even higher. Part of the increased ash content may derive from inorganic materials associated with the organic materials adsorbed during the treatment operation. An additional part of the ash could result from silt or other fine mineral matter in the suspended solids which deposited on the activated carbon particles. This is especially true for the packed bed used in Phase III, where precipitate from chemical treatment could escape from the filter. A large ash build-up could be a problem for any operation in which the carbon is to be repeatedly reactivated. If the increased ash content has any deleterious effects on the sorptive characteristics of the activated carbon, a factor which has not yet been completely defined, it may be necessary to provide for acid washing of the carbon, either before or after regeneration.

Particle Size

The particle size distributions for the dried spent carbon and fresh carbon from Phase II are given in Table 7. The spent carbons from both packed and expanded beds underwent a slight reduction in average particle size. For the expanded beds, the carbon in the lead columns for the two systems remained essentially unchanged in particle size distribution, while the carbons in the two trailing columns showed rather significant decreases in the plus-30 fractions, with corresponding increases in the plus-40 fractions. The reason for this is not known. The estimated average particle sizes calculated from the sieve analyses suggest that somewhat more particle attrition occurred in the packed beds, with a change in average particle size of about 0.08 mm taking place. This result is reasonable since the carbon used in the expanded bed had been subjected to crushing and sieving operations which would reduce the weaker particles, leaving a greater percentage of abrasion-resistant particles in the carbon charged to the bed. In addition, the gentle agitation of the particles in the expanded bed during normal operation was much less severe than the vigorous agitation required during cleaning of the packed beds. As has already been noted, it was necessary to subject the packed beds to the cleaning operation much more frequently than the expanded beds.

Iodine Adsorption

The activities of the spent carbon samples as measured by Iodine adsorption are listed in Table 8. These values give some

TABLE 7

Particle Size Analysis of Carbon
Before and After Use

| | | Fresh Carbon | | Dried Spent Carbon From Columns | | | |
|---|---|---|---|---|---|---|---|
| | | | | Packed Bed | | | |
| | | | | PCU1 | PCU2 | PCF1 | PCF2 |
| Percent Retained on U.S. Sieve No. | 16 | 28.3 | 18.4* | 20.4 | 22.5 | 24.5 | 24.2 |
| | 20 | 36.1 | 37.8 | 28.9 | 32.3 | 28.8 | 28.4 |
| | 30 | 23.8 | 28.4 | 33.5 | 31.5 | 31.2 | 32.6 |
| | 40 | 9.5 | 13.6 | 15.4 | 12.5 | 14.5 | 13.6 |
| | 50 | 1.1 | 1.2 | 1.8 | 1.2 | 1.0 | 1.2 |
| | Pass | 0.2 | 0.6 | <0.1 | <0.1 | <0.1 | <0.1 |
| Average size, mm | | 0.99 | 0.92 | 0.85 | 0.89 | 0.88 | 0.87 |
| | | | | Expanded Bed | | | |
| | | | | ECU1 | ECU2 | ECF1 | ECF2 |
| Percent Retained on U.S. Sieve No. | 16 | 0.8 | 0.4* | 1.7 | 1.7 | 1.2 | 1.0 |
| | 20 | 4.3 | 1.0 | 4.2 | 2.8 | 3.0 | 2.4 |
| | 30 | 64.2 | 59.8 | 60.8 | 46.1 | 58.2 | 48.8 |
| | 40 | 27.4 | 35.4 | 32.7 | 42.6 | 35.2 | 42.5 |
| | 50 | 2.3 | 3.2 | 0.6 | 6.8 | 2.4 | 5.3 |
| | Pass | 1.0 | 0.2 | <0.1 | <0.1 | <0.1 | <0.1 |
| Average size, mm | | 0.67 | 0.64 | 0.66 | 0.61 | 0.65 | 0.62 |

*Analysis on sample from second bag.

TABLE 8

Iodine Number of Virgin and Spent Carbon

| Sample Identification | Dried Sample | Devolatilized Sample |
|---|---|---|
| PHASE II | | |
| Virgin Carbon | 1050 | |
| PCU 1 | 551 | 815 |
| PCU 2 | 638 | 845 |
| PCF 1 | 526 | 816 |
| PCF 2 | 633 | 850 |
| Virgin Carbon | 1053 | |
| ECU 1 | 440 | 764 |
| ECU 2 | 526 | 792 |
| ECF 1 | 446 | 762 |
| ECF 2 | 538 | 797 |
| PHASE III | | |
| PC 1 | 629 | 878 |
| PC 2 | 710 | 883 |
| PC 3 | 800 | 945 |
| PC 4 | 888 | 1035 |
| EC 1 | 612 | 860 |
| EC 2 | 670 | 891 |
| EC 3 | 782 | 936 |
| EC 4 | 873 | 1020 |
| EC Carryover | 936 | 1085 |

indication of the remaining adsorption capacity of the spent carbons. The dried samples of spent carbon from Phase II exhibited iodine numbers roughly half of that of the virgin carbon. For each of the four experimental systems in Phase II, the spent carbon from the first column had a lower iodine number than that from the second. Further, the spent-carbon samples from the packed beds had somewhat higher iodine numbers than those from the expanded beds. The differences in the iodine numbers of about 100 for the dried samples and about 50 for the carbonized samples suggest some possible differences in the adsorptive behavior of the carbon particle from the packed and expanded beds.

The additional crushing and sieving operations to which the carbon used in the expanded beds was subjected probably reduced the percentage of more friable particles. The more friable particles, on the other hand, generally contain larger pores, which would be less subject to blocking by adsorbed molecules. The particles remaining in the 20x40 range used in the expanded beds would then consist largely of the relatively stronger particles with a finer pore structure. It is possible that adsorbed organic matter concentrated at the pore openings more effectively restricts penetration of the iodine molecules into the smaller pores of the spent carbon recovered from the expanded beds. Carbonizing and destruction of the adsorbed molecules would tend to reduce this restricting effect, resulting in smaller differences in the iodine numbers for the carbons from the packed and expanded beds. This result suggests that on reactivation the activity of the carbons, at least as measured by the iodine number, would again be essentially equal.

Spent-carbon samples from both the packed and expanded beds in Phase III showed increasing iodine numbers from the first to the fourth contactor. This expected result is in agreement with adsorption and volatile matter data discussed earlier. Since, in contrast to Phase II, the same carbon was used in both packed and expanded beds, there was not a large difference in iodine numbers of samples from the two beds. For dried samples, the expanded bed was lower by an average value of 23; for devolatilized samples the difference was only 9.

## Extractions

Some studies were performed to provide preliminary information on the character of the organic materials adsorbed on the spent carbon. Determination of the precise nature of the adsorbed materials was considered to be much beyond the scope of the project; thus, the studies were limited for the most part to chloroform extractions followed by preliminary separations by column chromatography. Some tests were conducted to determine the presence of carbonyl compounds in the extracts.

The most simple analysis was that performed on a drained sample of the spent carbon from the Phase I studies. The carbon was extracted with chloroform and subsequently with methanol to

yield fragrant oily brown residues upon evaporation of the solvents. The total weight of the residues amounted to somewhat over 10% of the weight of the carbon sample from which it was extracted.

More detailed analyses were performed on the carbons recovered from the four different adsorption systems studied in Phase II. Samples of each of these batches of carbon were first extracted with chloroform by the procedure described in Standard Methods.[9] The extracts were then evaporated at 60°C under reduced pressure. The weights of the extracts so obtained are listed in Table 9.

Chromatography

All of the residues extracted from the Phase II carbon samples were viscous, dark brown oils exhibiting a strong earthy odor, similar to that extracted from the Phase I carbon. In an attempt to further classify these extracts, a 7.61-gm sample of the residue from the packed-bed unfiltered-feed carbon was placed on a column of chromatographic grade active alumina, in chloroform. A total of 55 fractions was taken from the column, all of 25-ml volume except for a final acetic acid strip. The solvent systems used for the fractionations are listed in Table 10. The amounts of material eluted from the various solvent systems are also listed in Table 10, along with the weight percentages of the total eluent represented by each fraction. The total amount of extract recovered from the chromatographic column in the 55 fractions was 7.2 gm, or approximately 95% of the amount of the chloroform extract originally applied to the active alumina.

All of the 55 fractions taken from the chromatographic column were either brown or yellow-brown oils. The original strong earthy odor of the chloroform extract was eluted from the column with the first ten fractions; very little of this odor remained with the subsequent fractions, all of which exhibited in varying degree the burnt-sugar odor characteristic of lignin pigments. All of the fractions involving acetic acid appeared to have undergone some reaction which reduced them to virtually insoluble resins. These resins accounted for about 43% of the material eluted.

The first four fractions with chloroform as the solvent showed some tendency to form crystals. The crystal-like substances formed were not well defined, but rather had a sticky and impure appearance. To explore this behavior further, these four fractions (1.71 gm) were combined and chromatographed on active alumina with chloroform. A total of 25, 10-ml fractions was taken. Three of these fractions were combined and crystallized from a one to one mixture of chloroform and n-heptane, resulting in 392 mg of very sticky crystals. The crystals were then re-dissolved in chloroform and chromatographed again as described above, with a total of 25 more 10-ml fractions being taken. Three of these fractions were combined and chromatographed in the same fashion, for 25 additional 10-ml fractions. Upon combining four of the fractions and crystallizing them, 80 mg of very sticky crystal again resulted, with the same appearance as the crystals formed

TABLE 9

Chloroform Extracts from the Phase II Spent Carbon

| Sample Identification | Carbon Sample Weight, gms | Extract Weight, gm | Extract, % by Weight |
|---|---|---|---|
| PCU | 807.2 | 40.273 | 4.99 |
| PCF | 857.1 | 43.096 | 5.03 |
| ECU | 913.5 | 47.936 | 5.25 |
| ECF | 985.8 | 52.607 | 5.34 |
| Total packed bed | 1664.3 | 83.369 | 5.02 |
| Total expanded bed | 1899.3 | 100.543 | 5.29 |
| Total unfiltered feed | 1842.9 | 95.703 | 5.19 |
| Total filtered feed | 1720.7 | 88.209 | 5.12 |

Average extract, % by weight = 5.16

TABLE 10

Chromatographic Fractionation of the Chloroform Extract from the Phase II Packed-Bed Unfiltered-Feed Carbon

| Fraction Nos. | Solvent System | Solvent Volume Ratio | Extract Eluted, gm | % of Total Eluent |
|---|---|---|---|---|
| 1-12 | Chloroform | - | 2.391 | 33.2 |
| 13-19 | Chloroform: Ether | 1:1 | 0.194 | 2.7 |
| 20-23 | Ether | - | 0.060 | 0.8 |
| 24-29 | Ether: Ethyl Acetate | 1:1 | 0.062 | 0.9 |
| 30-32 | Ethyl Acetate | - | 0.019 | 0.3 |
| 33-38 | Ethyl Acetate: Ethanol | 1:1 | 1.093 | 15.2 |
| 39-47 | Ethanol | - | 0.255 | 3.5 |
| 48-54 | Ethanol: Acetic Acid | 9:1 | 2.737 | 38.0 |
| Strip | Acetic Acid | - | 0.392 | 5.4 |
| | Totals | | 7.203 | 100.0 |

in the four original fractions. Since this procedure was unable to sufficiently purify the crystalline material, the tests were terminated

Carbonyl Compounds

To test for the presence of carbonyl-group-containing substances in the extracts from the activated carbon, a sample of the extract from the packed-bed unfiltered-feed carbon was treated with 2, 4-dinitrophenylhydrazine (DNP), which forms specific compounds with carbonyl groups. The resulting dinitrophenylhydrazones (DNPH's) are very useful for characterizing the carbonyl-group-containing compounds originally present. The DNPH's which formed in treating the extract with DNP were isolated and recrystallized. Thin-film chromatographic measurements suggested that the DNPH's so obtained were virtually one pure compound. Further, the spectrum obtained for this DNPH (in ethanol) in the ultraviolet region suggested that it was an aliphatic DNPH. From measurement of the absorbance of this material at a wave length of 361 mμ ($\lambda_{max}$ for aliphatic DNPH), and using a range of literature values for the molar absorptivity of several aliphatic DNPH compounds of from 21,400 1/mol-cm to 23,600 1/mol-cm, the molecular weight range for the isolated DNPH was calculated as being 274.1 to 305.3. Because the basic DNP moiety has a molecular weight contribution of 196.1, it can be concluded that the remainder of the DNPH molecule has a weight of from 78.0 to 109.2. This corresponds to a carbon chain of from 6 to 8 carbon atoms.

## GENERAL DISCUSSION

Experimental results have shown that the expanded-bed and packed-bed adsorption systems are very nearly equivalent with regard to removing soluble organic material from secondary effluent. The packed-bed system is more effective for removal of suspended solids, but the clogging that results from these solids causes high pumping pressures and the need for frequent cleaning of the carbon. Neither configuration gave solids removals from trickling-filter effluent sufficient to eliminate the need for further treatment when a high clarity water is desired. When the feed contains suspended materials, but a high degree of removal of these materials is not required, the expanded-bed system appears to have definite advantages over the packed-bed system.

It is difficult to interpret the advantage of the expanded bed precisely in terms of capital and operating cost savings because these costs will be affected by the amount and character of suspended material in the feed water. Since comparison of soluble-organic removal by the two bed configurations was considered the most important objective of this study, experimental work was limited to one trickling filter plant. Care must be used in extrapolating suspended-solids and pressure-drop results to other plants, especially activated sludge plants. Some general qualitative and rough quantitative size and cost comparisons for the two contactor configurations can be made, however.

An expanded-bed system can produce more treated effluent than a packed-bed system of equivalent size because of less down-time for the carbon cleaning operation. From the results of the present study, it is estimated that an hour per day would be required and about an hour's production of treated water would be utilized during the backwash following air scrubbing. If the expanded-bed system required no cleaning, its actual production would be 109% of a packed bed designed for the same flow rate. The expanded bed will require some cleaning, but at much less frequent intervals. Results from another carbon study conducted on an activated sludge effluent with low suspended solids substantiate the need for daily backwash of a packed carbon-contactor.[3] The backwash water requirements were somewhat lower than an hour's production.

The elimination of frequent carbon cleaning results in a savings in operating labor for the expanded bed. For very small plants with little automation the labor cost saving could be appreciable. For plants of 10 mgd (or greater) capacity the cost reduction probably would only be about 0.1¢/1,000 gal.

The higher pressures resulting from packed-bed operation have several effects on costs. The most obvious effect is an increase in pumping power requirements. Assuming a conservatively high average pressure difference of 20 psi for the packed bed over the expanded bed, the cost difference would be about 0.2¢/1,000 gal. This is a very minor factor. The pumps for the packed bed would be larger, but this also is probably not significant. The most important

effect of pressure is on the type of contacting equipment that can be used. For an expanded-bed system it should be possible to construct open-top tanks, probably of concrete. From the experimental results, a height about double the unexpanded height of carbon should be sufficient. It is likely that the carbon would be divided into several beds in series to obtain some measure of countercurrent contacting and to give a reasonable equipment height. A similar series arrangement for a packed-bed system would also probably be employed. With packed-bed systems there is a question of whether open tanks could be used or whether closed pressure vessels would be necessary. The latter would be several times the cost of open vessels because they must be constructed of steel and must be relatively small in diameter. For all but very small plants, parallel contactor-systems would be necessary. From the pressure data shown in Figure 11 and 29, open tanks do not appear practical for this particular effluent because of the excessive freeboard that would be required as solids accumulated on the carbon. For a wastewater of lower suspended solids content, open tanks might be applicable, especially if the flow rate per unit area were decreased. This would have to be determined, however, for each particular case. Detailed consideration of the costs of contactors was not within the scope of this study.

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